LRTAP WORKSHOP NO. 5

"BROWN WATERS" : RELATIVE IMPORTANCE OF EXTERNAL AND INTERNAL SOURCES OF ACIDIFICATION ON CATCHMENT BIOTA

REVIEW OF EXISTING KNOWLEDGE

MARCH 1986

Sponsored by:
Environment Canada
Department of Fisheries and Oceans

Prepared by:
ESSA Environmental and Social
Systems Analysts Ltd.

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Canada

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Prepared for:
Environment Canada
and
Department of Fisheries and Oceans

By:
Michael L. Jones
David R. Marmorek
Barb S. Reuber
Peter J. McNamee
Linda P. Rattie

ESSA Environmental and Social Systems Analysts Ltd.,
#102 - 66 Isabella Street
Toronto, Ontario
M4Y 1N3

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EXECUTIVE SUMMARY

Acid rain - its sources, distribution and effects, continues to be an issue surrounded by a great deal of controversy, both scientific and political. Much of the debate centers around questions concerning the contribution to surface water acidity of local, catchment derived sources relative to more distant, atmospheric sources. Recently, Environment Canada and the Department of Fisheries and Oceans funded a review of existing knowledge relevant to this issue. The review, presented in this document, is based on an assessment of past and current literature, and a 3 day workshop involving 38 scientists, including hydrologists, soil and water chemists, and biologists.

The review concentrates on four, closely related questions:

1. Are there important local sources of surface water acidity that are not governed by atmospheric deposition of mineral acidity, and how important are these sources relative to external, atmospheric sources, especially on an extensive scale?
2. What role do wetlands play in surface water acidification, both as sources of acidity and as systems that modify the chemistry of water arriving from upland or atmospheric sources?
3. In what ways is surface water chemistry affected differently by organic acids than by mineral acids?
4. Do biota respond differently to changes in surface water chemistry associated with organic acidity than to changes associated with mineral acidity?

There is good evidence that the acidity of surface waters can be influenced substantially by local sources. Low pH surface waters exist whose acidity is largely organic in nature - organic acidity is almost exclusively derived from local sources. In addition, it is clear that local land management activities can profoundly influence surface water chemistry. Of particular significance are activities that affect the vegetative structure of a catchment (and thus element cycling) or the amount and distribution of wetland habitat.

There is no evidence, however, that the widespread observations of increased acidity in surface waters subject to relatively high levels of acidic deposition can be explained by local land management activities. Data from regional surveys invariably show much stronger associations between mineral acid anions (or estimated acid deposition rates) and

surface water pH or acid neutralizing capacity (ANC), than between organic anions and pH or ANC. These studies point compellingly towards a primary role for atmospheric deposition in the control of surface water acidity in high deposition areas.

There is a growing body of evidence that documents the important role of wetlands in catchment hydrology and water chemistry. Wetlands tend to act as attenuators of runoff, sinks for incoming mineral acids, and sources for organic acids and organically complexed metals such as aluminum. The long term role of wetlands as sinks for acidity is not well understood, nor is their importance on an regional scale. Most of the current understanding of the role of wetlands comes from work on peatlands (fens and bogs); relatively little is known about the role of other types of wetlands.

The chemistry of organic acids in surface waters is very different from that of mineral acids. Two of the most important differences are:

1. that organic acids can be an important pH buffer for waters in the pH 4.5-5.5 range; and
2. that organic ligands have a strong tendency to chelate metals such as aluminum, and as a consequence increase their solubility.

There remains considerable uncertainty concerning the influence of the specific chemical composition of dissolved organic carbon (DOC) on these properties of organic matter. The critical question might read: "Are there spatial or temporal differences in the character of DOC that give rise to measurable (and ecologically significant) differences in these properties?"

From the standpoint of biotic effects, there is a great deal of evidence to show that biota respond very differently in low pH surface waters whose acidity is predominantly organic than in those dominated by mineral anions. These differences appear to be largely due to the chelating effect of organic ligands on aluminum, a process that substantially reduces the toxicity of this metal. On the other hand, very little is known about the direct effect of organic acids on biota. Once again, a central question is whether the character of DOC significantly influences its effects (both direct and indirect) on biota.

Finally, a recurring theme throughout this review is the importance of short term (seasonal) variations in hydrological, chemical and biological conditions. Seasonal variations in the rates of various biological processes have a profound influence on the chemistry of surface waters. Patterns of surface water chemistry can in turn interact in sometimes subtle but significant ways with seasonal variations in the behaviour of a particular species of biota. In a similar vein, the importance of distinguishing between loadings and concentration is stressed: constituents which have high concentrations in the runoff only during low flow periods may in fact contribute relatively little to a catchment's annual element mass balance.

While this review documents that much is known about the processes that control surface water acidity and its interaction with biota, it would be an understatement to say that uncertainties still remain. At the workshop, a number of research needs were clearly identified that demand attention if the questions posed by this review are to be adequately answered. To achieve complete consensus among a group of 38 scientists on the order of priority for this research would be an unrealistic goal. Nevertheless, there was little disagreement that especially high priority should be attached to four particular needs or approaches:

1. A rich body of data already exists, relevant to both this and many other issues, that has not been adequately analysed (in some cases not at all). Before committing substantial resources to further, survey oriented data collection, every effort should be made to ensure that the best possible use is made of existing information.

2. Field and laboratory studies should be conducted to determine the necessary degree of characterization required to adequately describe DOC. This would involve determining the spatial and temporal degree of variation in the character of DOC, and establishing whether these differences are ecologically significant (in terms of their effect on biota).

3. More research is needed on the role of wetlands in controlling surface water chemistry, and as important ecosystems in their own right. Of greatest need is knowledge that would allow us to generalize both regionally and across a range of wetland types.

4. Finally, few existing models of surface water acidification include organic acids. There is a great need to develop simple, but still realistic models that include organic acids, and can be used to link current scientific understanding to the development of policy.

ACKNOWLEDGEMENTS

We would like to express our appreciation to all those in attendance for contributing their ideas and energy to the stimulating discussions during the workshop. This report is largely the result of their hard work and expertise. We have made every effort to accurately represent the views expressed by these individuals at the workshop and subsequently as reviewers of a draft version of the report. Nevertheless, we accept full responsibility for any ideas or views that have been misrepresented in the text that follows.

Special thanks go to Tom Clair and Dick Peterson for organizing the workshop and providing all of us who attended the opportunity to work together on this fascinating and important problem. We also wish to thank the staff of the Huntsman Marine Laboratory for cheerfully providing everyone at the workshop with comfortable accommodations and good food.

This report could not have been produced without the many varied skills and extreme diligence of Ms. Teri Dykeman and Ms. Josephine Cassidy. We are also most grateful to them, and to Gene Szram for drafting Figures 2 and 3.

LIST OF PARTICIPANTS

Workshop Chairman	
Tom Clair	Water Quality Branch Moncton, New Brunswick
ESSA Ltd. (Workshop Facilitators)	
Peter McNamee	Biota
Barb Reuber	Surface Waters
David Marmorek	Uplands
Michael Jones	Wetlands
Biota	
Stephen Beauchamp	Canadian Wildlife Service Halifax, Nova Scotia
Joseph Freda	McMaster University Hamilton, Ontario
Geoff Howell	Water Quality Branch Moncton, New Brunswick
Gilles Lacroix	Dept. Fisheries & Oceans St. Andrews, New Brunswick
Don McNicol	Canadian Wildlife Service Ottawa, Ontario
Dick Peterson	Dept. Fisheries & Oceans St. Andrews, New Brunswick
Wesley White	Dept. Fisheries & Oceans Halifax, Nova Scotia
Surface Waters	
Rick Bourbonniere	National Water Research Institute Burlington, Ontario
Floyd Elder	National Water Research Institute

	Burlington, Ontario
Robert Gershey	Seakem Oceanography Ltd. Dartmouth, Nova Scotia
Les Hulett	Environment Newfoundland St. John's, Newfoundland
Steve Kahl	University of Maine Orono, Maine
Joseph Kerekes	Canadian Wildlife Service Halifax, Nova Scotia
Dominique Levesque	Environment New Brunswick Fredericton, New Brunswick
Tom Pollock	Water Quality Branch Moncton, New Brunswick
John Underwood	Nova Scotia Environment Halifax, Nova Scotia

Uplands

Paul Arp	University of New Brunswick Fredericton, New Brunswick
William Hendershot	McGill University Ste-Anne-de-Bellevue, Quebec
Ray Hesslein	Dept. Fisheries & Oceans Winnipeg, Manitoba
Ingrid Kessel-Taylor	Lands Directorate Ottawa, Ontario
David Lam	National Water Research Institute Burlington, Ontario
Taumey Mahendrappa	Canadian Forestry Service Fredericton, New Brunswick
Hans Martin	Atmospheric Environment Service Downsview, Ontario

J. Gordon Ogden III	Dalhousie University Halifax, Nova Scotia
Simon Visser	Laval University Quebec City, Quebec

Wetlands

Tom Clair	Water Quality Branch Moncton, New Brunswick
Eville Gorham	University of Minnesota Minneapolis, Minnesota
Hinrick Harries	Mt. Allison University Sackville, New Brunswick
Harry Hirvonen	Environment Canada Dartmouth, Nova Scotia
Bruce LaZerte	Environment Ontario Dorset, Ontario
Clayton Rubec	Lands Directorate Ottawa, Ontario
Bill Shotyk	University of Western Ontario London, Ontario
Colin Taylor	Trent University Peterborough, Ontario
Noel Urban	University of Minnesota Minneapolis, Minnesota

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I INTRODUCTION

The ecological effects of industrial emissions, long range atmospheric transport and subsequent deposition of acidic substances, has been the subject of an enormous amount of debate over the past decade, both scientific and political. Acidic deposition is believed to be responsible for widespread changes in surface water chemistry in northern Europe and northeastern North America, changes which have in at least some cases caused undesirable impacts on water quality and biota (Harvey et al. 1981, MOI 1983). There is not universal consensus, however, that emissions of "acid gases" from industrial sources, and their subsequent transport and deposition onto distant watersheds, are responsible for these changes (Rosenqvist 1978, Krug and Frink 1983). Proponents of alternative explanations for changes in surface water chemistry in these areas suggest that there are important natural sources of acidity in watersheds, and that these sources can be greatly influenced by land management activities within the watershed of interest. Clearly from a policy perspective, it is critical to discriminate unequivocally between these two alternatives, or at least to identify their relative importance.

In both Canada and the United States, a great deal of research has been carried out, and is ongoing, that is intended to shed light on this issue. The research ranges from detailed laboratory investigations of the processes involved in surface water acidification and its biological effects, to extensive surveys intended to correlate water quality parameters to watershed or atmospheric factors, or to estimate current levels of aquatic damage. In the presence of such a diverse set of research activities and results, it is often difficult if not impossible for scientists (and policy makers) to keep abreast of the "state of the science". The challenge to both people managing research and those responsible for doing it is to ensure that their activities:

- capitalize upon results from ongoing research in both North America and Europe;
- maintain their relevance to the major issues of concern;
- are well coordinated, with integration across disciplines, methodologies and agencies; and

- can be used as much as possible to provide insights into the relevant issues on an extensive (i.e., broad geographic) scale.

To help meet these challenges, Environment Canada and the Department of Fisheries and Oceans have contracted ESSA Ltd. to conduct a review of the relative importance of mineral versus organic acidity to the process of surface water acidification, and to facilitate a workshop attended by leading researchers in this field. A first draft of this document was prepared for review prior to the workshop, which was held in St. Andrews, New Brunswick from Dec 3 to 5, 1985. The draft was circulated to all workshop participants in November, and was used as a framework for discussions at the workshop. This document presents a revised review, incorporating ideas and recommendations for research that emerged at the workshop.

Organization of the Review

Not surprisingly for an issue of such great political prominence, there is an enormous amount of literature on acidic precipitation and its effects. Numerous comprehensive reviews of the subject already exist (e.g., Harvey et al. 1981, MOI 1983, U.S. EPA 1984). Our purpose in this review was not to repeat, even in part, these efforts. Instead, we have attempted to synthesize the issues and knowledge surrounding the topic of interest here into a set of structured hypotheses which served to guide the workshop discussions. The procedure was used recently in a similar workshop whose focus was the importance of snowmelt episodes to surface water acidification (Marmorek et al. 1984).

In the broadest sense, the review was intended to consider alternative sources of surface water acidity (Figure 1), with emphasis on the contrast between local (e.g., catchment derived) and external (e.g., atmospheric deposition) sources. More specifically, we set out to examine the following questions:

1. Are there important local sources/causes of changes in surface water acidity that are not governed by atmospheric deposition of mineral acidity?
2. How important are these sources of acidity relative to mineral acidic deposition, especially on an extensive scale?
3. Do land management activities, such as forestry, influence these internal sources of acidity in a manner that offers an

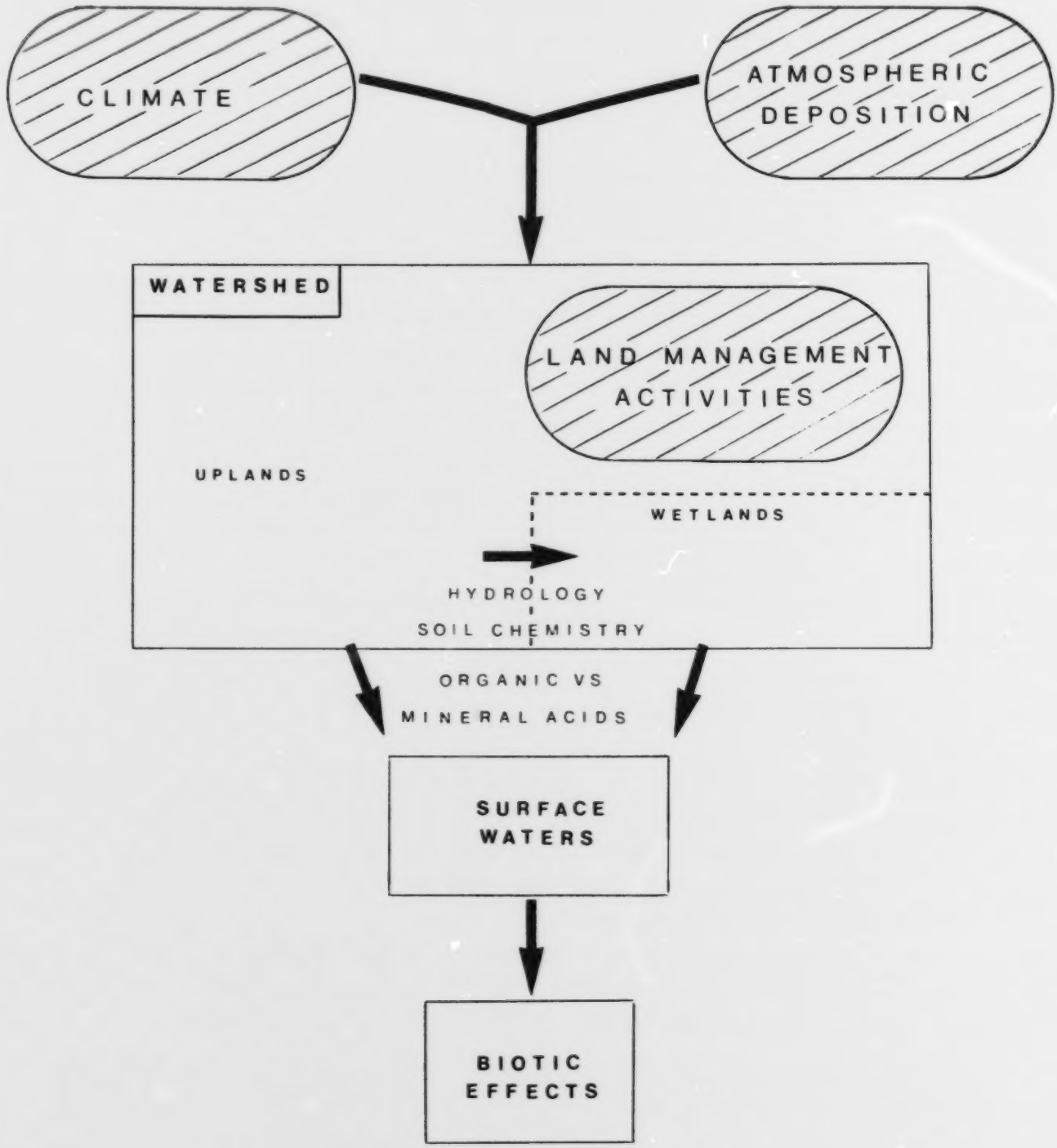


Figure 1. A simple conceptual framework for the issue of external versus internal sources of acidity and their effects on biota.

alternative explanation for historical trends in surface water chemistry?

Since much (though by no means all) locally derived acidity is organic in nature, while atmospheric sources contribute primarily mineral acidity, two further questions of interest were:

4. Does organic acidity interact chemically in surface waters in a different manner to mineral acidity, especially with aluminum?

5. Are biota affected differently by internally generated acidity and by externally derived acidity?

Until recently, most research on the effects of atmospheric deposition of mineral acids on surface waters has focussed on upland, rather than wetland areas. Because of the importance of wetlands as sources of organic acidity, and in light of the large differences between uplands and wetlands in their chemical interactions with runoff, an additional question has been given explicit attention:

6. What is the role of wetlands in surface water acidification, and how is this role affected by either atmospheric deposition or land management activities?

To organize both the review and the discussions that took place at the December workshop, we recast these questions as a set of four structured hypotheses (Marmorek et al. 1985), dealing with upland hydrology and chemistry; wetland hydrology and chemistry; surface water chemistry; and biota. For the most part, Hypothesis 1 addresses questions 1-3 above, Hypothesis 2 considers question 6 and Hypotheses 3 and 4 deal with questions 4 and 5 respectively. Each hypothesis contains a set of linkages which attempt to describe specific processes or interactions relevant to the overall hypothesis. These hypotheses and their respective linkages provide a framework for examining the current state of knowledge in a focussed and relevant manner. The hypotheses are combined into an overall conceptual model in Figure 2.

In the remainder of this report, we present a detailed assessment of the current understanding of each hypothesis, based on a review of recent literature, and on the results of discussions with researchers in this field, primarily at the December workshop. We conclude with a brief section summarizing the research recommendations that emerged out of the workshop discussions.

Before turning to the detailed discussions that follow, the reader

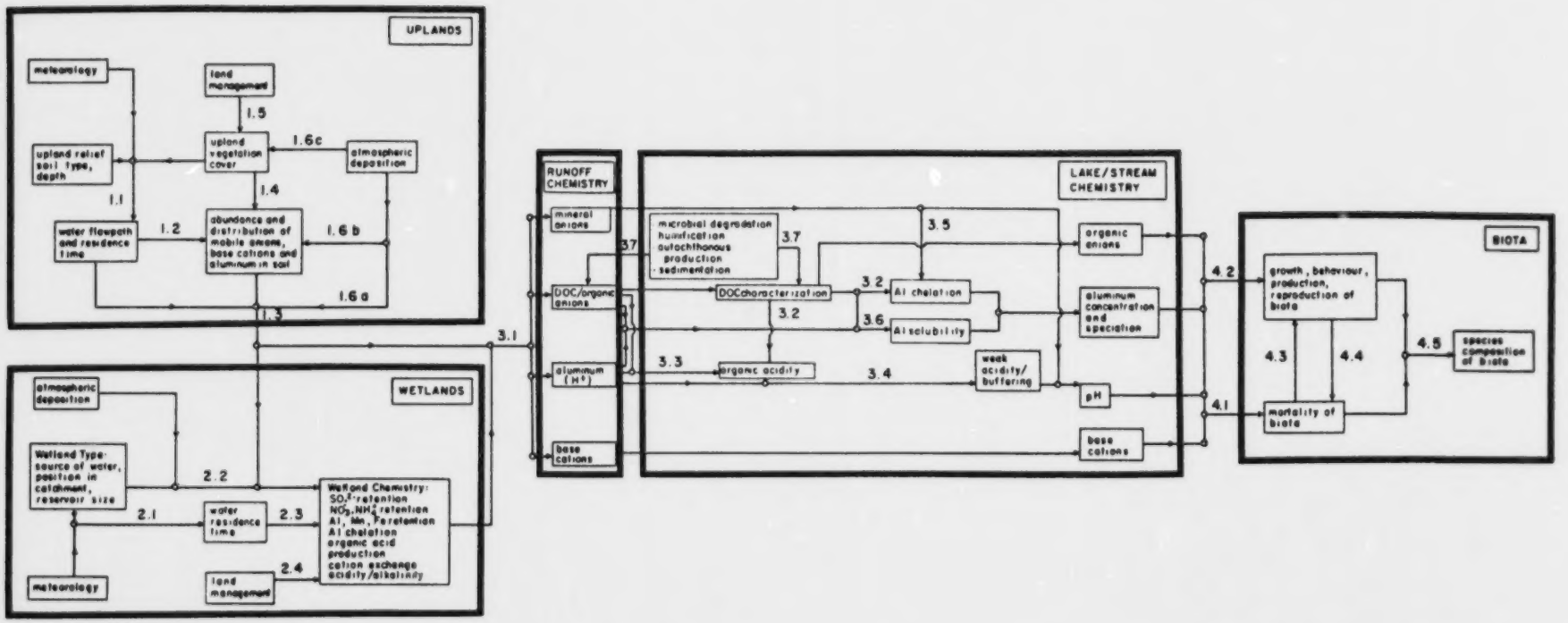


Figure 2. Detailed conceptual model of the hypotheses and linkages discussed in Section II.

should be cautioned that a relatively large number of references are made in the text to unpublished manuscripts and personal communication. While this may leave some readers feeling uneasy about the assertions that are based primarily on these sources, we have opted to include them so as to allow this document to be as "up-to-date" as is possible. Our purpose is to report on the current thinking on the issues discussed herein, and to highlight the need for further research in particular areas, not to provide an uncontroversial review of only those findings that are universally accepted.

II STRUCTURED HYPOTHESES

HYPOTHESIS 1: THE CHEMISTRY OF RUNOFF FROM UPLAND AREAS IS THE RESULT OF INTERACTIONS BETWEEN FOUR MAJOR FACTORS: WATER FLOWPATH AND RESIDENCE TIME; THE ABUNDANCE, MOBILITY AND DISTRIBUTION OF ANIONS, BASE CATIONS AND ALUMINUM IN THE SOIL; THE LEVEL OF ATMOSPHERIC DEPOSITION OF STRONG ACIDS AND THEIR PRECURSORS; AND LAND MANAGEMENT ACTIVITIES.

Linkages:

1.1-1.3 In upland areas, the chemistry of runoff water is determined by the abundance and mobility of anions, base cations and aluminum in different soil horizons and by the flowpath and residence time of water in these horizons. Water flowpath and residence time are in turn determined by the interaction of meteorology (precipitation, air temperature) with watershed features (vegetation cover, watershed relief, soil type and depth).

1.4 Growth of vegetation affects soil chemistry by plant assimilation of base cations and mobile anions, by production of organic acids from plant metabolism or decomposition, and by (indirectly) affecting rates of mineralization (e.g., ammonification) and chemical transformations (e.g., nitrification).

1.5 Land management activities (particularly logging, burning, changes in vegetation and fertilization) and forest regrowth can significantly affect the chemistry of runoff water, via changes in either hydrology (Figure 2, links 1.1 and 1.3) or soil chemistry (links 1.4 and 1.3).

1.6 Strong acids deposited from the atmosphere may affect runoff chemistry through three major pathways:

a. direct additions to surface water (link 1.6a).

b. direct impacts on soil chemistry (link 1.6b), which affect runoff chemistry (link 1.3); and

c. direct (link 1.6c) or indirect (link 1.6b) impacts on vegetation, with consequent changes in soil chemistry (link 1.4) and hydrology (link 1.1) that ultimately affect runoff chemistry (link 1.3).

Discussion

Hypothesis 1 consists of two fundamentally different sets of statements. Linkages 1.1 to 1.3 are generally well accepted principles of hydrology and soil science. Linkages 1.4 to 1.6 on the other hand are less well understood and more controversial. It is not the purpose of this review to offer a comprehensive examination of the empirical and theoretical basis for the first set of Linkages, though some discussion is necessary in order to establish a basis for examining the second set in detail.

Important Hydrological and Soil Processes

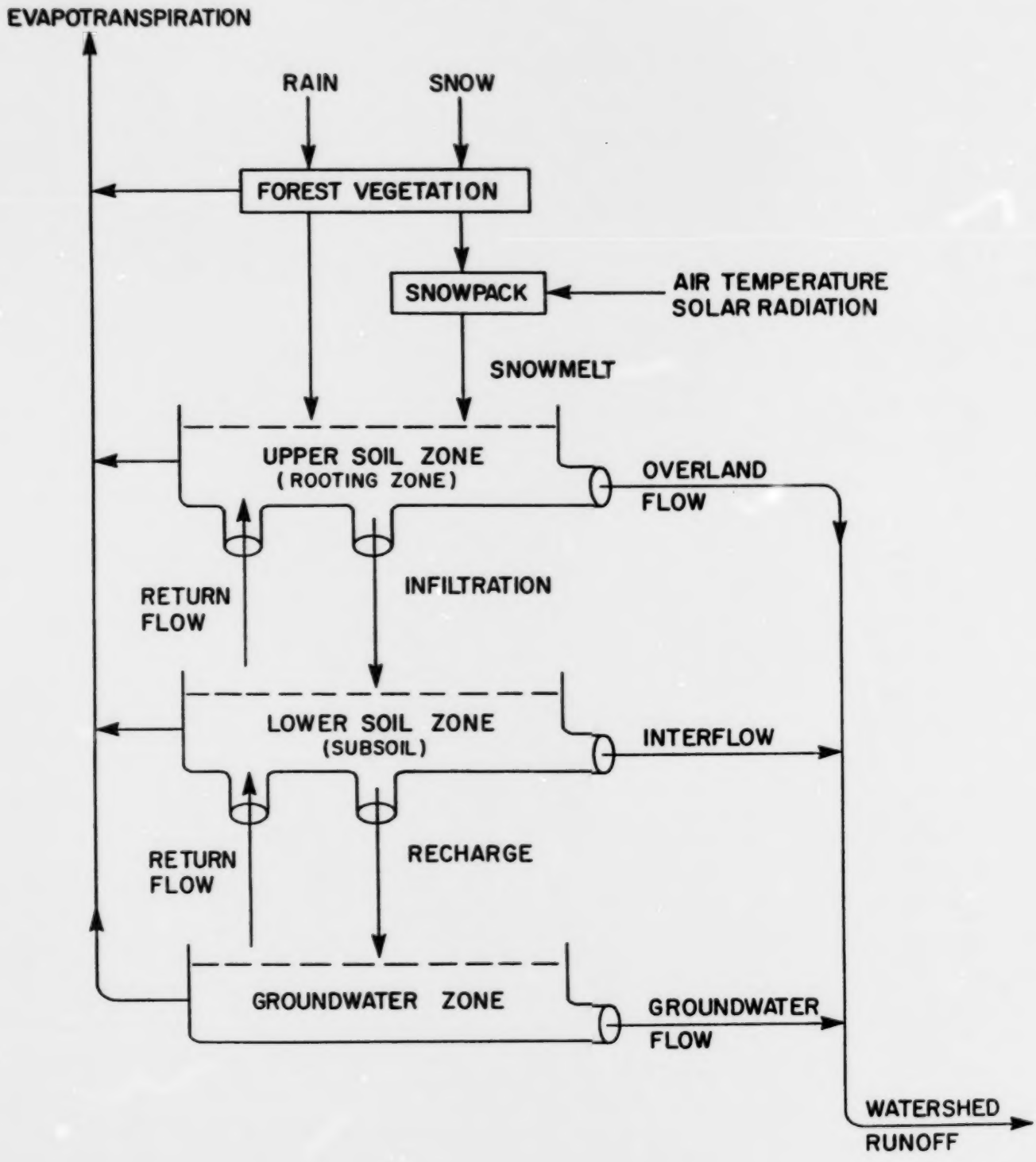
Linkage 1.1 IN UPLAND AREAS, WATER FLOWPATH AND RESIDENCE TIME ARE DETERMINED BY THE INTERACTION OF METEOROLOGY (PRECIPITATION, AIR TEMPERATURE) WITH WATERSHED FEATURES (VEGETATION COVER, WATERSHED RELIEF, SOIL TYPE AND DEPTH).

Linkage 1.2 THE FLOWPATH OF WATER AND ITS RESIDENCE TIME AFFECTS THE ABUNDANCE AND DISTRIBUTION OF MOBILE ANIONS, BASE CATIONS AND ALUMINUM WITHIN THE SOIL PROFILE.

Linkage 1.3 THE CHEMISTRY OF RUNOFF WATER IS DETERMINED BY THE LEVEL OF ATMOSPHERIC DEPOSITION (AS ALTERED BY CANOPY AND GROUND VEGETATION), THE FLOWPATH AND RESIDENCE TIME OF WATER IN DIFFERENT SOIL HORIZONS, AND THE ABUNDANCE AND MOBILITY OF ANIONS, BASE CATIONS AND ALUMINUM IN THOSE HORIZONS.

It is widely believed that the most important factor determining the chemistry of surface water is the flowpath taken by water in reaching the stream channel. Since the chemical composition of soils (and water) at different depths varies enormously, the water that flows only through surface horizons will have radically different chemistry from water derived from deeper horizons. Similarly, water that has passed through wetland areas may have quite different constituents than water derived from upland areas (Hendershot et al. 1984, Bache 1984, Taylor and Pierson 1984). Hypothesis 2 describes wetland processes and contrasts these with processes dominant in the upland zone. Here we focus on upland processes alone.

Figure 3 provides a useful schematic for considering water flowpaths. Beginning at the top of the figure, the interaction of precipitation with forest vegetation (both in the canopy and on the ground) can affect both the quantity of throughfall (Mahendrappa and Kingston 1982), and the chemical characteristics of throughfall and stemflow (Mahendrappa 1974 and 1983, Johannes et al. 1984). In addition, the amount and rooting depth of vegetation will affect the rates at which water percolates through surface horizons to the lower soil zones. The relative importances of the flows from the different soil horizons shown in Figure 3 vary seasonally, with important consequences for surface water chemistry. These seasonal variations are described in detail by Hendershot et al. (1984), and the following discussion paraphrases their



Conceptualized water quantity model (Bobba and Lam, 1984)

Figure 3. Schematic diagram of water flows in a watershed. Modified from Bobba et al. 1985

text.

During low flow periods, water reaching streams is derived from the deeper soil horizons (baseflow or groundwater flow) and has spent a relatively long time in contact with the soil matrix. During precipitation or snowmelt events, stormflow (also called quickflow) predominates. Stormflow typically spends far less time in contact with soils, and sometimes does not contact deeper soil horizons at all. Stormflow can derive from at least three sources. First, precipitation onto completely saturated soils can result in overland flow which only contacts surface horizons rich in organic matter. Second, return flow results when the water table rises due to displacement by percolating water in adjacent areas. Such water has been in contact with deeper horizons, but passed through surface horizons last before reaching the stream. This type of flow is often associated with the displacement (piston flow) of "old" water that has spent a long time in soils by "new" water from precipitation. Hendershot et al. (1984) describe conditions under which these types of flow might result. Finally, under special circumstances, such as frozen soils, steep slopes, or high rainfall intensity precipitation rates may exceed infiltration rates, resulting in so called Hortonian overland flow. Streamwater derived from this type of flow is probably similar to that resulting from precipitation onto saturated soils, in that it only comes in contact with surface, organic soil horizons.

Organic acids accumulate most strongly in the organic surface horizons of the soil, due to the large volume of inputs to this zone (i.e. throughfall, stemflow and mineralization). The greatest total loading of organic acids to surface waters generally occurs during storm or snowmelt events in which substantial overland or return flows move through this zone. However, the relative increase in flow through surface horizons may exceed the relative increase in leaching of organic acids, resulting in a decrease in concentrations of organic acids in surface waters. Examples of field studies measuring organic acidity during storm and snowmelt events are presented below for Linkage 1.4.

In most catchments, the watershed characteristics that influence hydrology (link 1.1) will be sufficiently heterogeneous that any or all of the above-described flows may occur, at various locations or times of the year. The key point is that the chemistry of surface waters in a

catchment will strongly reflect the dominant flowpath taken by water before reaching the stream or lake. In fact, the most common means of determining the flowpath of water in a catchment for different types of events is to infer the pathway from information on changes in streamflow and surface water chemistry during the event combined with knowledge of the chemical effect of different soil horizons (see Marmorek et al. 1984 for a discussion of this approach).

Movement of water through particular soil zones leaches ions, and thus affects the pool of ions remaining (link 1.2). Budgeting of the pools in each zone must consider not only these leaching losses, but also the inputs and outputs due to other processes. Clearly, any discussion of the relative importance of particular factors in particular zones (e.g., the effects of forest growth on soil chemistry in organic surface horizons) must be held in the context of the total set of inputs and outputs. To lay the foundation for such a discussion, is is useful to document (Table 1) the major inputs and outputs of water, carbon, base cations and aluminum for each of the four zones in Figure 3.

To assess the effect of water movement on the pools of compounds remaining in particular zones one must consider what proportion of the pool is mobile. This question is best considered in terms of the phases in which compounds appear in soils. Four phases are generally recognized:

1. The Occluded Phase. All inorganic and organic compounds which do not disintegrate within a specified time interval (e.g., decades) are considered to be part of this phase.
2. The Accessible Phase. Compounds in this phase are subject to ongoing chemical change (e.g., weathering).
3. The Exchange Phase. Compounds which are surface sorbed but can participate in cation and anion exchange reactions are considered to be in the exchange phase.
4. The Solution Phase. Most of this report concerns chemical reactions which occur to ions and organic acids in this phase, such as complexation, cation or anion uptake by plants, changes in the speciation of aluminum, and movement of mobile aluminum and organic acids from the watershed to surface waters. Also, measurement of soil pH refers to the equilibrium between the exchange and solution phases.

Though Linkages 1.1 to 1.3 are generally accepted, our state of knowledge is far from being able to predict quantitatively what the effect of these processes are on surface water chemistry. For example,

Table 1: Processes controlling movement of water, carbon, base cations and aluminum through and from forest soils.

ZONE	SUBSTANCES	INPUTS	PROCESSES	OUTPUTS
surface zone (ground or snowpack)	water	snow, direct rainfall, throughfall, return flow from organic surface horizon		saturated overland flow through snowpack
	base cations, aluminum	minor, except when dusty		
organic surface horizon	water	meltwater or rain from surface, return flow from rooting zone		evapotranspiration, quickflow
	carbon	litterfall, root growth, stemflow, throughfall		decay (CO_2 losses), particulate and dissolved organics in quickflow, leaching of soluble organics to rooting zone
	base cations	leaching from surface, mineralization, return flow from rooting zone, stemflow, throughfall		leaching to rooting zone or quickflow, cation uptake by plants
	Al	leaching from surface, return flow from rooting zone, mineralization		leaching to rooting zone or quickflow, uptake by plants
rooting zone	water	infiltration from organic surface horizon, return flow from subsoil		evapotranspiration, interflow, return flow to LFH
	carbon	root growth		leaching to surface water and subsoil (minor), CO_2 losses
	base cations	leaching from LFH, weathering, return flow from subsoil, mineralization		leaching to surface water and subsoil, return flow to LFH, cation uptake by plants
	Al	leaching from LFH, weathering, return flow from subsoil, mineralization		leaching to surface water and subsoil, return flow to LFH, uptake by plants
subsoil	water	recharge from rooting zone		return flow to rooting zone, baseflow to surface waters
	carbon	minor leaching from rooting zone		minor constituent of baseflow
	base cations, Al	leaching from rooting zone, weathering		return flow to rooting zone, leaching in baseflow, adsorption (Al)

Driscoll (1984) points out that there is no consensus among scientists on which compounds (e.g., kaolinite, aluminum trihydroxide, soil organic matter) control dissolved aluminum concentrations (see also Arp and Ouimet 1985). This makes calculation of the amount of aluminum leached from soils quite uncertain. Methods which estimate the relative contributions of groundwater, intermediate flow and overland flow to surface waters are extremely useful to scientists attempting to understand the interaction of water flowpaths and soil chemistry. In particular such methods can be used to verify the predictions of hydrochemical models (see Bobba et al. 1985). Such methods include lysimeter measurements of meltwater and soilwater, analytical methods to separate hydrographs into stormflow and baseflow components, chemical budgeting of conservative substances, and use of both stable and radioactive isotopes (reviewed in Marmorek et al. 1985).

The Roles of Vegetation, Land Management and Acidic Precipitation

Linkage 1.4 GROWTH OF VEGETATION AFFECTS SOIL CHEMISTRY BY PLANT ASSIMILATION OF BASE CATIONS AND MOBILE ANIONS, BY PRODUCTION OF ORGANIC ACIDS FROM PLANT METABOLISM OR DECOMPOSITION, AND BY INDIRECTLY INFLUENCING THE RATE OF NITRIFICATION.

Vegetation withdraws cations and anions from the soil profile through roots and redistributes them to the surface horizons through litterfall. These processes do not directly affect the absolute amount of ion leaching, but control the distribution of individual ionic species. This in turn affects whether particular soil horizons will acidify or maintain an equilibrium with the base-producing weathering process (U.S. EPA 1985).

Growth of forests leads to an accumulation of nutrients in wood and foliage biomass each year. A larger quantity of nutrients is cycled from the soils, through tree foliage, and back to the soils in throughfall and litterfall. The yearly accumulation results in a net acidification of the soil due to uptake of excess cations over anions, which the tree balances by exporting H^+ ions through the roots (Nilsson et al. 1982). Even if no excess cations are absorbed, however, soil acidification can occur as a result of increased production of organic acids via decomposition and

plant/microbial metabolism. Together, these processes can result in acidification of some soils comparable to or beyond that of yearly leaching by acidic deposition (Alban 1982, Nilsson et al. 1982, Johnson and Richter 1984).

There remains considerable uncertainty regarding the changes in natural acidification that occur as the forest ages. The most widely held views are similar to the hypotheses of Nilsson et al. (1982), who outlined the sensitivity of soil acidification to the growth rates of trees (site factors), the level of forest management (e.g., thinning), and the age of the forest. One model, as formulated by Nilsson et al. (1982) projects moderate rates of acidification during ages 0 to 20 of a pine stand, high but decreasing rates during ages 20-40, and very low rates from age 40 on. They estimated that within a fast growing pine forest in the middle third of a sixty year rotation, the net rates of acidification as a result of excess cation accumulation in trees would be equivalent to 1 m of pH 3.8 rain per year. Rates of acidification in slow growing, unmanaged pine forests (typical of many regions in Southern Norway subject to acid deposition) were much lower however, and less than the hydrogen loading currently received from atmospheric deposition. Harriman and Morrison (1980) found catchments with coniferous forests had far more acidic streamwater then did adjacent, unforested catchments. They proposed that increased uptake of basic cations in the forested catchment accounted for this difference.

The model used by Nilsson et al. (1982) does not account for production of organic acids. Though soil acidification through this mechanism is difficult to quantify, it is expected that it would vary over the age of the stand in a manner similar to the pattern described above (i.e., maximum organic acid production during the middle third of the rotation).

It is difficult to predict the effect of forest growth on the concentration of organic acids in surface waters. Though production of organic acids should increase as forests grow, the amount of water reaching the stream is likely to decrease. This suggests that the concentration of organic acids in surface waters should rise. Changes in stream pH as a stand ages have not been documented, however. There is a need for analyses of existing data on the organic acidity of streams draining different aged stands.

Two processes associated with organic decomposition are ammonification (a neutralizing process) and nitrification (an acidifying process). During snowmelt, Rascher et al. (in press) observed significant increases in nitrate (and H^+) in meltwater moving across the forest floor. They attributed these increases to mineralization and nitrification, but pointed out that their results may have been confounded by disturbance of the forest floor during the installation of the lysimeters used to collect meltwater. In general, the higher levels of nitrate found in surface waters in winter and early spring than at other times are thought to be due to the greatly reduced uptake of nitrate (produced from mineralization and nitrification) by living vegetation during dormant periods.

The role of nitrate during snowmelt has also been studied in detail in Canada. Increases in surface water nitrate concentrations have been observed during snowmelt at Lac Laflamme, Quebec (Papineau 1984), and in the Muskoka-Haliburton and Turkey Lakes areas of Ontario (LaZerte and Dillon 1984, Jeffries and Semkin 1983 respectively). Preliminary results from studies by English et al. (1985) in the Turkey Lakes watershed indicate that virtually all of the snowpack nitrate is flushed through the terrestrial system (i.e. no retention). Nitrate peaks within Ontario are generally of less severity than those in the Adirondacks, which may offer opportunities for interesting inter-regional comparisons of nitrate sources during snowmelt.

Another important issue is the effect of organic and mineral acid production on aluminum levels and mobility in the soil. This issue falls under Linkage 1.4, since it is another means by which vegetation growth affects soil chemistry. Many northern temperate soils are subject to the podzolization process, in which aluminum (as well as other metals such as iron) are leached by organic acids from upper to lower soil horizons (Driscoll 1984). Driscoll (1984) points out that though podzolization redistributes aluminum, it moves very little aluminum from watershed soils to surface waters. Also, aluminum still remains abundant in surface horizons. For example, Driscoll et al. (1985) (cited in Rascher et al. in press) found that on a molar basis, aluminum was the dominant cation within the forest floor of the Hubbard Brook Experimental Forest (much of it associated with organic matter). Mineral acids deposited

from the atmosphere can theoretically mobilize substantial quantities of aluminum that were either previously precipitated within the soil during podzolization or held on soil exchange sites (Cronan and Schofield 1979, U.S. EPA 1985), and acidic surface waters do tend to have higher concentrations of total aluminum (data reviewed in Driscoll 1984).

How does the level of organic acids in the soil affect the mobilization of aluminum, particularly in catchments subject to acid deposition? Both theoretical and field approaches have been used to address this question. Recently, Arp and Ouimet (1985) used a computer model to examine influences on the total soluble aluminum concentration in a synthetic soil solution. Three factors were considered: the soil solution pH, the presence or absence of organic ligands, and the solid phase controlling the activity of Al^{3+} in solution. The results indicated that all three factors played a role. The model generated two particularly interesting predictions:

1. The total organic aluminum concentration tends to be stable and pH-independent between pH 3.5 and 8.0, when the total water-soluble organic acid concentration is held constant.
2. Organic ligands increase aluminum solubility by complexation reactions and render the pH a poor predictor of total soluble aluminum in soils.

These predictions imply that processes which increase water soluble organic acid production will increase the concentration of aluminum in soil solutions. Hendershot et al. (1984) found that in the seven soils they studied (across three forested basins) the contribution of aluminum from litter horizons was dependent on the degree of decomposition. More highly-decomposed horizons had lower pH and higher levels of reactive (though not necessarily mobile) aluminum.

Although soil type may be important to aluminum concentrations in soil solutions, the hydrological properties of the basin largely determine aluminum concentrations in the stream. In the study cited above, two of the three basins contained very shallow soils over bedrock while the third contains deeper soils in the lower part of the basin. During storm events the streams in the first two basins showed large increases in the concentration of reactive aluminum, reaching levels similar to the upper soil horizons (i.e., 460-635 ug/L). There were also substantial increases in the proportion of fast-reacting complexed aluminum. The

third basin's stream aluminum concentrations increased only slightly during storm events (up to 43 ug/L) and continued to resemble concentrations observed in deeper soil horizons. Aluminum speciation was virtually identical before and during the rainfall event. These inter-basin differences appeared to be due more to differences in flowpaths than to differences in soil type. These results raise the question: with respect to aluminum mobilization, are differences among watersheds in the rate of vegetation growth (and therefore differences in organic acid production and aluminum mobilization) as significant as differences among watersheds in soil thickness, drainage and terrain?

Winter weathering and decomposition can substantially increase the concentration of total aluminum in soil solutions. Hendershot et al. (1985), studying a Quebec catchment, found 3-4 times greater total aluminum concentrations in groundwater than in the snowpack, apparently due to winter accumulations of weathering products in the soil. Rascher et al. (in press) compared total aluminum concentrations in the snowpack and forest floor leachates in an Adirondack basin. They found 14-fold increases in total aluminum as water passed through the surface horizons, which they attributed to mineralization reactions within the forest floor. Throughfall and stemflow can also be substantial sources of aluminum, which may cause erroneous inferences if not specifically considered (Mahendrappa, pers. comm.).

In conclusion, there is evidence for at least at some sites that the production of organic acids increases aluminum solubility and mobility. Upland areas are generally considered to be a source of aluminum while wetland areas are thought to be sinks (but see link 2.5). However, there are very few sites with sufficient data to allow an assessment of these questions on an extensive basis. Measurements of aluminum speciation are needed in soil solutions and streams across contrasting soils and over all four seasons. Further measurements of the decay rates of humic and fulvic compounds, and the complexation constants of organic anions with iron, manganese and aluminum in real soil solutions would also be of considerable value.

Linkage 1.5 LAND MANAGEMENT ACTIVITIES (PARTICULARLY LOGGING, BURNING, CHANGES IN VEGETATION AND FERTILIZATION) AND FOREST REGROWTH CAN ALTER VEGETATION COVER SUFFICIENTLY TO SIGNIFICANTLY AFFECT THE CHEMISTRY OF RUNOFF WATER, VIA CHANGES IN EITHER HYDROLOGY (LINKS 1.1 AND 1.4) OR SOIL CHEMISTRY (LINKS 1.3 AND 1.4).

Linkage 1.6 STRONG ACIDS DEPOSITED FROM THE ATMOSPHERE MAY AFFECT RUNOFF CHEMISTRY THROUGH THREE MAJOR PATHWAYS: a) DIRECT ADDITIONS TO SURFACE WATER (LINK 1.6A). b) DIRECT IMPACTS ON SOIL CHEMISTRY (LINK 1.6B), WHICH AFFECT RUNOFF CHEMISTRY (LINK 1.3); c) DIRECT (LINK 1.6C) OR INDIRECT (LINK 1.6B) IMPACTS ON VEGETATION, WITH CONSEQUENT CHANGES IN SOIL CHEMISTRY (LINK 1.4) AND HYDROLOGY (LINK 1.1) THAT ULTIMATELY AFFECT RUNOFF CHEMISTRY (LINK 1.3).

> "Factors affecting surface water acidification, including natural, cultural (that is, land-use changes, forest harvesting), and atmospheric deposition, are unclear. Given the great concern over aquatic effects of acid deposition, a comprehensive research effort into mechanisms of terrestrial-aquatic transfer (both hydrological and chemical) is badly needed, not only to clarify the roles of various factors in surface water acidification but also as a prelude to implementation of effective mitigation techniques".
>
> (Johnson and Reuss 1984)

As suggested by this quotation from a recent conference on acidic precipitation, there remains considerable controversy regarding the relative importance of land management activities (Linkage 1.5) and atmospheric deposition of strong acids (Linkage 1.6) in controlling surface water acidification. In the remainder of this discussion, we examine the evidence that either supports or contradicts these two linkages, both on local and extensive spatial scales.

Land management activities, particularly removal of forest, or changes in forest vegetation structure can obviously have important hydrological implications (Jeffrey 1970). Perhaps most important, growth and/or changes in vegetation will alter the quantity of precipitation reaching surface waters via changes in rates of interception (Mahendrappa and Kingston 1982) and evapotranspiration (Penman 1967). For example, Swank and Douglas (1974) observed a 20% reduction in stream flow in a North Carolina watershed, after conversion of the forests in the area from deciduous hardwoods to pine. As well, changes in forest cover may change the moisture retention characteristics of surface horizons, and therefore total water yield (Mahendrappa 1982). Reduced water yield will

tend to concentrate conservative substances in the runoff.

Forest land management activities, such as logging, burning and scarification may also alter the soil surface structure and composition (including the amount of litter present, and possibly even topography on a small scale), thereby leading to changes in evaporation, infiltration, and horizontal flow. All of these changes may therefore have important implications for the output of Linkage 1.1, namely water flowpaths and residence times in various watershed compartments.

The effects of land management activities on soil chemistry are more complex and controversial. Scientists supporting the position that surface water acidification is not due to atmospheric deposition but rather to natural processes and land management activities, point to the fact that soils in so called sensitive catchments are highly acidic themselves (Rosenqvist 1978, Krug and Frink 1983, Noggle et al. 1984). The exchangeable acidity of soils such as podzols far exceeds the amount of acidity deposited from the atmosphere. Proponents of this view argue that the small additions of acidity from the atmosphere cannot have a significant impact on runoff chemistry, because it is added to already highly acidic soils. Instead, they argue that the processes discussed earlier (Linkage 1.4), related to changes in watershed vegetation, are responsible for the observed increases in surface water acidity. These authors suggest that the deforestation that occurred several decades ago probably decreased surface water acidity and that these systems are now returning to a "natural" state.

Most evidence from field studies tends to contradict this hypothesis. For example, Likens et al. (1970) found that deforestation led to five fold increases in stream H^+ and 40 fold increases in stream NO_3^-. This was apparently due to increased nitrification in the absence of forest vegetation. In support of their hypothesis, Likens et al. (1970) cited a study by Nye and Greenland (1960) which found that growing vegetation reduced soil pH and repressed nitrification. On the other hand, Delorme et al. (1984) analyzed the historical pollen and diatom species composition in Kejimkujik Lake, Nova Scotia, and found a change in diatom species indicative of increased pH to have occurred at approximately the time of deforestation (mid-1800's). Their methods have been questioned, however, due to significant DOC differences between Kejimkujik Lake and

the lakes for which the pH-diatom relationship used were developed (Howell and Lakshminarayana in prep.) DOC is also known to affect diatom species composition (see Hypothesis 4).

There appears to be good evidence that forest growth leads to soil acidification, as discussed above under Linkage 1.4. This does not necessarily imply acidification of surface waters. Nilsson et al. (1982) pointed out two important differences between acidity from rainwater and that released from roots:

1. Atmospheric deposition of hydrogen ions exhibits a markedly fluctuating and stochastic behaviour, whereas root uptake of cations shows a smooth seasonal variation. As a result, rainwater is likely to have less soil contact.
2. Hydrogen ions in precipitation are introduced at the surface, whereas protons produced by root uptake emerge in intimate proximity to the exchange surface or weathering mineral from which the base cation was derived, and is therefore very likely to become attached to the exchange surface or participate in weathering reactions.

The debate cited above is mostly concerned with long term acidification on the scale of decades. Noggle et al. (1984) suggest that atmospheric deposition cannot account for changes in runoff chemistry on short (episodic) time scales either. They provide evidence for a catchment in North Carolina that incoming acidity does not reach the soils in significant quantities during storm events, due primarily to canopy interception. Instead they propose that observed declines in runoff pH and increases in aluminum are due to stormwater only passing through surface organic soil horizons, thus carrying large amounts of weak organic acidity and associated soluble, complexed aluminum (see Hypothesis 3, link 3.2). The principal thrust of their argument is based on the contention that most of the acidity in runoff during the storm events is weak organic acidity, and thus cannot be attributed to external sources.

Recommendations for research on the effects of changes in upland vegetation center on analysis and synthesis of existing data from calibrated watersheds with experimental perturbations. This includes the U.B.C. Research Forest in British Columbia, the Nashwaak Experimental Watershed Project in New Brunswick, 3 IHD watersheds in Nova Scotia, the Coweeta watersheds in North Carolina, and Hubbard Brook in New Hampshire. Monitoring of experimental watersheds should continue, as long term

records are necessary for testing these hypotheses. Comparisons of the runoff chemistry in deciduous and coniferous sites (particularly with respect to organic acidity) would shed light on the effects of changes in forest type. Finally, the development of simple, transferable models of forest biomass and cycling of nutrients (e.g., McGrath 1985) would assist in the prediction of soil solution pH levels and anion concentrations. Testing of these models in field situations should proceed in parallel with their development.

If changes in land use, not atmospheric deposition, are the principal cause of surface water acidification, then one would generally expect to see the following:

1. the principal anions associated with runoff acidity would be organic, because this is the primary form of acidity associated with surface soil horizons; and
2. the amount of acidity (mineral or organic) entering runoff should be independent of the amount of acidic deposition occurring in the catchment in question, provided acidic deposition and land use are not closely geographically correlated.

Some land management activities may contribute acidity accompanied by nitrate rather than organic anions, such as planting of N-fixing alders (Mahendrappa, pers. comm.) or deforestation (Likens et al. 1970, discussed above). Therefore, condition #1 above will not always apply. It is nevertheless worth examining the extent of organic acidity, since many hypothesized acidification mechanisms involve increases in organic anions. Organic anions have been shown to contribute significantly to the acidity of surface waters (Kerekes 1977, Glover and Webb 1979, Hemond 1980, Beck et al. 1974, Underwood et al. 1985). On the other hand, numerous studies have provided evidence that, in sensitive areas receiving acidic deposition, mineral anions (especially sulphate) typically dominate the chemistry of runoff and surface waters (examples in Overrein et al. 1980, Harvey et al. 1981, MOI 1983). For example, Cronan et al. (1978) found that sulphate was the predominant anion in forest soil leachates in a New England sub-alpine forest, an area receiving substantial sulphate deposition. In contrast, bicarbonate and organic anions dominated the leachate chemistry of soils in areas receiving much less mineral acid deposition (e.g., Pacific Northwest forests).

Analyses of extensive data sets appear to show reasonably good asso-

ciations between estimated sulphate deposition and lake sulphate levels (Thompson and Hutton 1985, Kelso et al. in press, Rapp et al. in press), and between lake sulphate and lake acid neutralization capacity (ANC) (Henriksen 1980), Harvey et al. 1981, Kelso et al. in press). On the other hand, there does not appear to be a good association, on an extensive basis, between lake organic acidity (as estimated from DOC and pH, method of Oliver et al. 1983) and lake ANC (Jeffries et al. in press). LaZerte and Dillon (1984) also present evidence that the rate of cation leaching (measured as annual cation export) from soils is correlated with acid deposition rates. This is consistent with Wright's (1983) model of surface water acidification due to atmospheric deposition.

The issue of natural versus anthropogenic acidification thus appears to reduce to a question of whether one is comparing individual cases or extensive, regional information. There is little doubt that surface waters exist whose chemistry is measurably influenced by natural sources of organic acidity (examples cited above). As well, ample evidence exists to show that vegetation type and amount can exhibit a major influence on the production of organic acids (Harriman and Morrison 1980, Noggle et al. 1984, Cronan and Aiken 1985) and thus that changes in vegetation resulting from land management activities might affect surface water chemistry. On an extensive scale, however, the evidence points compellingly towards a prominent role for atmospheric deposition in controlling surface water acidity in sensitive areas.

An additional factor that has tended to confound this issue concerns seasonality. The production of organic acidity has been shown to exhibit pronounced variation seasonally, both in terms of quantity (Cronan and Aiken 1985, LaZerte and Dillon 1984) and quality (Visser 1984, R. Bourbonniere, pers. comm.). LaZerte and Dillon (1984), however, show that while organic acidity predominates in Plastic Lake during summer low flows, its contribution is relatively minor during high flow periods and thus annually. This is a key point - during much of the open water season, measurements of chemical inputs to a lake may often suggest that organic acids are very important. During spring high flow (snowmelt) and fall storms, however, sulphate is the dominant anion. In terms of total loadings to the lake on an annual basis, sulphate inputs far exceed those

of organic anions. In some areas (i.e. the Adirondacks) nitrate inputs may also exceed those of organic anions.

The most widely accepted mechanism by which atmospheric deposition affects runoff acidity is via the so-called mobile anion concept (Seip 1980). Introductions of an anion, such as sulphate, that is not retained by watershed soils, requires that some cation be released by the watershed's soils to maintain charge balance in runoff. In soils with very low base saturation, the cations released are typically acidic (H^+, Al^{3+}). Henriksen (1980) proposed a simple model which assumed that only acidic cations were leached by anthropogenically derived sulphate. More recently, Henriksen (1982) and Wright (1983) have suggested that in fact some additional leaching of basic cations (Ca^{2+}, Mg^{2+}) is also stimulated by sulphate deposition, with the result that surface waters are less rapidly acidified, but soil base saturation is depleted. Johnson and Reuss (1984) support these "models" but point out that:

1. sulphate is adsorbed by many soils, thereby reducing (at least temporarily) its mobility; and
2. the rate of leaching of basic cations will depend strongly on base saturation, a factor which varies considerably among sensitive, acidic soils.

The sensitivity of soils (and thus surface waters) to acidic deposition thus depends on the sulphate adsorption capacity and base saturation of those soils (see also Arp 1983a). A better understanding is needed of sulphate uptake, soil adsorption/desorption and reduction/oxidation reactions, but primarily only to predict the short term responses of surface waters to acidic deposition. In the long term, most Canadian mineral soil watersheds appear to be in balance with respect to sulphur (i.e., input = output).

The other strong acid anion in acidic deposition, nitrate, is generally thought to be rapidly assimilated by vegetation in most sensitive regions (e.g., Harvey et al. 1981, MOI 1983), because nitrogen is a nutrient typically in short supply in these systems (Johnson and Reuss 1984). Nitrate may, however, be important as a mobile anion during winter and spring (Krause 1982), and especially during snowmelt periods (Schofield 1977, Galloway et al. 1980).

Non-acidic atmospheric deposition may also influence soil and runoff

acidity. This occurs via the "salt-effect" (Johnson and Reuss 1984), which describes a process whereby increases in the total ion concentration of a soil solution decreases its pH via soil ion exchange processes. Addition of neutral salts (e.g., sea salts) to soils of low base saturation will lead to replacement of the basic cation in solution with H^+ (or Al^{3+}). Johnson and Reuss (1984) point out that small changes in soil pH resulting from the salt effect can lead to substantial changes in runoff pH, due to the presence of high concentrations of dissolved CO_2 in soil water (a result of root respiration and organic matter decay). The CO_2 degasses when soil water becomes surface water, but solution pH will only change as a result of degassing if the alkalinity is positive.

Krug and Frink (1983) argue that, even if acidic deposition is contributing to runoff acidity, it is only replacing acidity that would otherwise be generated internally from the large pool of acidity already present in soils. They therefore suggest that decreases in atmospheric inputs will not significantly affect runoff pH, but that anthropogenic mineral acidity will be replaced by natural, mostly organic acidity. LaZerte and Dillon (1984) refute this hypothesis by showing that lakes in the vicinity of Sudbury, Ontario, where local sulphur deposition rates have declined during the past two decades, have exhibited significant decreases in lake sulphate concentrations and concomitant increases in pH. They also point out that the required increase in DOC to replace mineral acidity by organic acidity completely would be unreasonable in areas currently receiving high levels of sulphate deposition (for Plastic Lake at high flow, 35-40 mg/l DOC would be required to replace a typical sulphate concentration of 180 ueq/l , based on the Oliver *et al.* 1983 model).

To conclude this discussion, let us return to the initial statements of Linkages 1.5 and 1.6. The weight of the evidence, particularly on an extensive basis, suggests that Linkage 1.6 is valid for a large number of systems. Clearly, the degree to which atmospheric deposition is transported directly into surface waters as mineral acidity depends on a host of factors: hydrological, chemical and biological (Bache 1984, Johnson and Reuss 1984). Most soils have the ability to radically alter the chemistry of precipitation, especially if this water passes through both surface organic and deeper mineral horizons, thereby allowing the chemi-

cal processes of cation exchange, sulphate adsorption and mineral weathering, and the biological processes of assimilation and decomposition, to interact with the infiltrating water. Nevertheless numerous studies indicate that acid rain can and does lead to acid runoff, especially when the contact time between soil and water is relatively short.

There is also evidence that natural sources of acidity in catchments can make important contributions to surface water acidity. As LaZerte and Dillon (1984) assert, "the ubiquitous presence of dystrophic waters on the Canadian shield (Armstrong and Schindler 1971, Dillon, P.J., unpublished data) and in the Maritime provinces of Canada (Kerekes 1980) suggests that organic acids derived from waterlogged organic soils may be important contributions to the acidity of freshwater catchments in regions subject to high levels of acid deposition and elsewhere". There is also good evidence that land management activities which result in changes in catchment vegetation can influence this and other sources of acidity. Nevertheless, there is little evidence to support the assertion that land management activities overwhelm the effects of acid deposition on runoff acidity, and none exists on an extensive basis.

HYPOTHESIS 2: WETLANDS PLAY A CENTRAL ROLE IN BOTH THE HYDROLOGY AND WATER CHEMISTRY OF CATCHMENTS, PRIMARILY BY ACTING AS ATTENUATORS OF RUNOFF, SINKS FOR MINERAL ACIDITY AND SOURCES FOR ORGANIC ACIDITY.

Linkages:

2.1 Wetlands can have a major influence on the hydrology of a catchment, by acting as a source area under wet conditions and a storage area under drier conditions. The magnitude of a wetland's influence depends on antecedent meteorological conditions, the size of the reservoir, and its position in the catchment.

2.2 The water chemistry of wetlands can be greatly influenced by both atmospheric inputs and inputs from upland areas. The relative importance of these two sources of chemical inputs varies considerably among wetland types.

2.3 The residence time (or alternately the flushing time) of water in wetland areas exerts a substantial influence on the ability of wetlands to alter the chemistry of waters passing through them.

2.4 Land management practices can profoundly affect wetlands and their role in catchment water chemistry, particularly by altering the hydrologic balance of the catchment, and as a result draining or flooding new areas.

2.5 Wetlands alter the chemistry of water passing through them via a variety of processes. The most important of these are sulphate, nitrate, ammonium and metals retention; aluminum complexation; production of organic anions via decomposition; and ion exchange and assimilation.

Discussion

So far, discussion of the effects of atmospheric deposition and land management on runoff hydrology and chemistry has focussed on interactions with typically well drained, upland soils. As pointed out by LaZerte and Dillon (1984), however, there are vast numbers of lakes, ponds and streams in Eastern Canada and elsewhere whose chemistry is profoundly influenced by the presence of waterlogged soils in their catchments. These areas are commonly known as wetlands. In this section we focus on the interactions of atmospheric deposition and land management with wetlands, both in terms of effects on wetlands themselves, and on lakes and streams that depend at least in part on wetlands for water inputs.

As with all scientific disciplines, wetlands science is plagued by necessary jargon. It is not appropriate to provide a detailed glossary as part of this review, but a few definitions will be useful for the discussion that follows. Wetlands include all lands that are wet enough for

long enough periods of time to allow the development of vegetation (and associated processes) that is distinct from surrounding, well-drained areas. Wetlands are generally classified into at least five major categories (Tarnocai 1979): bogs, fens, marshes, swamps and shallow water areas. Bogs and fens are generally distinguished from the other three wetland types by the predominance of peat deposits within them. They are commonly referred to as peatlands.

Vast areas ($>10^8$ ha) of Canada and the USSR are covered by peatlands, and in the words of Gorham et al. (1984), they "are a large and vital component of the biosphere and are believed to play a significant role in the global cycles and geochemical balances of carbon, nitrogen and sulphur". Thus they almost certainly constitute a major "sink", at least temporarily, for inputs of mineral acids and other pollutants from the atmosphere. This discussion will focus on peatlands, due to their unusual chemistry (compared to upland soils).

The distinction between bogs and fens is described succinctly by Wells and Hirvonen (in prep.). They state, "Both ecosystems (bog and fen) may form in the same manner, i.e. through annual growth and accumulation of vegetation remains on poorly draining soils. However, bogs are nutrient-poor and ombrotrophic, receiving their nutrition supply solely from atmospheric sources (i.e. rainfall and atmospheric dust). Fens also receive nutrients from atmospheric sources but are nutrient-rich and minerotrophic; they receive additional nutrients via seepage waters from the adjacent upland soils. The dominant vegetation of the bog is Sphagnum mosses, dwarf shrubs and lichens, whereas that of the fen is predominantly sedges and grasses with some Sphagnum mosses".

While all types of wetlands described above can have important influences on dowstream surface water quality, the majority of the evidence discussed in this section comes from studies of peatlands. This is not intended to imply that only peatlands are deserving of attention as contributors to surface water chemistry that differ significantly from uplands. Instead, the emphasis reflects the much greater interest that has been directed towards the very unusual chemistry of peat dominated wetlands.

Linkage 2.1 WETLANDS CAN HAVE A MAJOR INFLUENCE ON THE HYDROLOGY OF A CATCHMENT, BY ACTING AS A SOURCE AREA UNDER WET CONDITIONS AND A STORAGE AREA UNDER DRIER CONDITIONS. THE MAGNITUDE OF A WETLAND'S INFLUENCE DEPENDS ON ANTECEDENT METEOROLOGICAL CONDITIONS, THE SIZE OF THE RESERVOIR, AND ITS POSITION IN THE CATCHMENT.

All wetlands, not just peatlands, can play a central role in the hydrology (and chemistry) of watersheds containing them. In fact, their importance is often disproportionately greater than their actual size relative to the total catchment area. Braekke (1981) found that 62% of the output water in the Storgama catchment in Norway was chemically altered by flow through peatlands, which occupied only 24% of the total catchment area.

It is well known that wetlands act as runoff source areas under wet conditions, and as storage areas and runoff attenuators under drier conditions (e.g., Bay 1969, Woo and Valverde 1981, Taylor and Pierson 1985). Which role (source area versus storage area) is played by the wetland depends critically on antecedent conditions, and on its morphometry (reservoir size). In a small, southern Ontario catchment, Taylor and Pierson (1985) found that in the early stages of spring snowmelt, when groundwater levels were high, the wetland had little unsaturated storage capacity, and thus that it had minimal effect on the hydrograph. Later in spring, as the system drained and drier conditions prevailed, the wetland became an important storage area and the runoff was greatly attenuated. In relatively wet regions such as the maritime provinces, the former situation probably predominates, except during mid-late summer.

Although these effects are commonly observed for wetlands on relatively short time scales (i.e., for individual events), Bay (1969) and Woo and Valverde (1981) found the wetlands they examined to have little effect on seasonal or annual runoff yields. Taylor and Pierson (1985), however, found that a wetland produced significantly less runoff than did upland areas on an annual basis. They suggested that the hydrological significance of wetlands on longer time scales depends on whether the area becomes hydrologically isolated from the regional water table during low flows due to the presence of impervious clay layers beneath the wetland. Boelter and Verry (1977) also note that so-called perched

wetlands can respond quite differently during low flow periods than wetlands connected to the regional water table, and suggest that this is due to the considerable water losses to evapotranspiration that occur in perched systems. Perched wetlands are probably uncommon on the shield but are often found in areas such as northern Minnesota where deeper soils (till and sand plains) prevail.

While the hydrological role of wetlands is perhaps well understood in principle, their significance on a regional scale is largely unknown. One key factor that should not be ignored when considering the hydrological (and chemical) importance of wetlands, especially on a regional basis, is the position of the wetland in the catchment. Estimates of the percentage of the total catchment's drainage that passes through wetland areas might greatly enhance the ability to interpret and predict the role of wetlands. Crude measures of this on a regional scale might be obtainable from topographic maps or aerial photographs.

There is also a serious shortage of good hydrological information (e.g., hydrograph data) on a regional scale for small catchments. It is these systems that are most likely to be hydrologically affected by wetlands. As well they tend to be the most sensitive to changes in chemical inputs. A better understanding is needed of the role of wetlands in these catchments on a regional basis, and on the temporal (episodic, seasonal and long term) aspects of this role.

Linkage 2.2 THE WATER CHEMISTRY OF WETLANDS CAN BE GREATLY INFLUENCED BY BOTH ATMOSPHERIC INPUTS AND INPUTS FROM UPLAND AREAS. THE RELATIVE IMPORTANCE OF THESE TWO SOURCES OF CHEMICAL INPUTS VARIES CONSIDERABLY AMONG WETLAND TYPES.

As mentioned earlier, peatlands are typically classified in terms of this key characteristic, bogs being principally controlled by atmospheric inputs and fens by upland inputs. Bogs are characteristically more acid than fens and have lower nutrient levels. Thus it is widely accepted that this Linkage is true. Of greater interest in the context of atmospheric versus upland sources of acidity for wetlands, is the issue of how the levels of input (making a bog or fen either ombrotrophic or minerotrophic) affect a wetland's sensitivity to mineral acid deposition.

Sensitivity can be characterized in a variety of manners, some of

which may result in very different classifications from others. For example, the chemical sensitivity of a system (resistance to chemical change) may be quite different from its biological sensitivity (vulnerability of certain species). In the present context, however, sensitivity refers to the ability of a system to resist change in pH, in the face of increased atmospheric and upland inputs of mineral acids.

Truly ombrotrophic bogs are typically highly acidic, even at sites where mineral acid deposition is low (Gorham et al. 1984, Sjors 1952). This is because the internal generation of organic acidity overwhelms internal neutralizing processes such as sulphur reduction and nitrate assimilation (see below), in the absence of minerotrophic inputs of alkalinity. Such systems will resist further pH change due to weak acid buffering of incoming mineral acids. On the other hand, rich fens have relatively high pH levels, and tend to resist pH change due to substantial bicarbonate buffering derived from minerotrophic sources. Poor fens tend to have intermediate pH values, and little or no bicarbonate alkalinity. Thus on theoretical grounds, it is these systems that would be expected to be most sensitive to mineral acid deposition.

The evidence to support this expectation comes from two sources, neither of which are direct. First, regional surveys of peatland pH typically reveal a bimodal distribution, with relatively few systems being found in the intermediate range from 5-6 (Gorham et al. 1984, Gorham pers. comm.). This might suggest that such systems rapidly shift from circumneutral to acidic status, so that not many are present at these intermediate values. Lakes and streams show a similar distribution across regions, and acid sensitivity is normally cited as the explanation.

The second source of indirect evidence comes from observations of the natural acidification process that occurs in peatlands (Gorham et al. in press). Examination of peat profiles from bogs indicates that peatlands undergo a natural acidification process as their minerotrophic inputs are reduced as a result of peat accumulation. The shift from circumneutral to acidic conditions appears to be relatively rapid.

Unfortunately, there is no direct evidence to support this expectation, since time series documenting peatland water chemistry changes in response to changes in mineral acid inputs do not exist. A key unanswered

question is whether poor fens would be able to resist acidification from mineral acid inputs by reducing incoming N and S (see link 2.5). Experimental acidification of a poor fen with mineral acids might provide extremely valuable insights into this process (and others). As well, the indirect evidence warrants strengthening, both by examining peat profiles from a number of sites throughout eastern North America and by conducting a regional survey of wetland chemistry. The latter approach might be facilitated by looking at Geological Survey data on peatland vegetation, and then inferring chemical conditions from the species composition of the site.

Linkage 2.3 THE RESIDENCE TIME (OR ALTERNATELY THE FLUSHING TIME) OF WATER IN WETLAND AREAS EXERTS A SUBSTANTIAL INFLUENCE ON THE ABILITY OF WETLANDS TO ALTER THE CHEMISTRY OF WATERS PASSING THROUGH THEM.

Once again, there are compelling theoretical reasons for believing this Linkage to be true. Since all chemical and biological reactions take time, it is reasonable to assume that in the limit the amount of chemical change resulting from the passage of water through a peatland will depend on the contact time of that water with the peatland's rather unusual chemical environment. Chemical and biological reactions do reach equilibria, however, and do so at widely contrasting rates, so the relationship between residence time and degree of chemical changes is by no means straightforward.

There is at present no direct evidence that could be used to quantify the role of hydrology on wetland chemistry. On the other hand, there is a great deal of evidence to support the contention that its role is a quantitatively important one. For example, it has been noted for several systems that the chemistry of waters leaving wetlands is very different during high flow than low flow periods (e.g., Kerekes et al. 1982, LaZerte and Dillon 1984, 1985, Taylor and Pierson 1984; see also links 2.5 and 3.1). As well, Urban et al. (in press) found that the proportion of sulphate retained in bogs across eastern North America appeared to decrease with increasing flushing rates. Since seasonal and regional variations in hydrology appear to substantially influence peatland water chemistry, possibly to the extent that their long term role in affecting downstream water chemistry is reduced (see link 2.5), a better

understanding of this key interaction is needed. Perhaps the most fruitful approach would be to use hill-slope hydrological techniques (e.g., stable isotopes) under varying hydrologic conditions to look at mixing and to quantify water residence times.

Linkage 2.4 LAND MANAGEMENT PRACTICES CAN PROFOUNDLY AFFECT WETLANDS AND THEIR ROLE IN CATCHMENT WATER CHEMISTRY, PARTICULARLY BY ALTERING THE HYDROLOGIC BALANCE OF THE CATCHMENT, AND AS A RESULT DRAINING OR FLOODING NEW AREAS.

There are a variety of land management activities that commonly take place in otherwise undisturbed catchments, and can have major impacts on wetlands. The impacts of some are direct and obvious, such as the drainage of peatlands for fuel extraction. Others have more subtle, but nevertheless major effects. For example, the removal of vegetation in upland areas (logging) could decrease catchment evapotranspiration rates and thus greatly increase runoff (Penman 1967). The net effect of all these activities is to alter the hydrologic balance of catchments such that either the total area of wetlands (fens) is changed or the seasonal pattern of wetland filling and drainage is modified. As documented elsewhere (links 2.3 and 2.5) such changes may have pronounced effects on downstream water chemistry. This Linkage is not well understood, and in view of the controversy surrounding the relative importance of land use changes and atmospheric deposition, deserves further investigation.

Linkage 2.5 WETLANDS ALTER THE CHEMISTRY OF WATER PASSING THROUGH THEM VIA A VARIETY OF PROCESSES. THE MOST IMPORTANT OF THESE ARE SULFATE, NITRATE, AMMONIUM AND METALS RETENTION; ALUMINUM COMPLEXATION; PRODUCTION OF ORGANIC ANIONS VIA DECOMPOSITION; AND ION EXCHANGE AND ASSIMILATION.

The variety of processes that combine to substantially alter chemistry of waters moving through wetlands are not very well understood. In recent years the acid precipitation problem has stimulated substantial advances in this area, but our understanding remains primarily descriptive rather than predictive. In the discussion of this Linkage, we briefly summarize in turn our current understanding of each of the major processes involved.

Sulphate Retention

A primary mechanism by which peatlands neutralize incoming mineral acidity is via biological assimilation and chemical reduction of sulphate. The presence of anoxic waters in most wetlands provides an environment that is conducive to this process. Bayley et al. (1985) added sulphuric acid to a fen in northwestern Ontario and found sulphate was largely retained (77% retention) on an annual basis. Sphagnum absorption appeared to be responsible for most of this retention. At Marcell bog in Minnesota, annual sulphate retention ranged from 36-93% over a four year period (N. Urban, pers. comm.). The extremely high retention rate in 1983 (93%, next highest 58% in 1981) was associated with an unusually dry year (annual water yield less than 50% of the 21 year average). LaZerte and Dillon (1985) found a Sphagnum swamp in the Plastic Lake catchment strongly retained sulphate annually, but their results may have been affected by the extreme dryness of the year in which their observations were made (a 1-in-15-year event). Hemond (1980) measured annual total sulphur retention in Thoreau's Bog in Massachusetts to be 77%. Retention of total sulphur will always be lower than sulphate retention due to the tendency for sulphate to be reduced to organic sulphur and partially exported in this form. Finally, at Moosepit Brook in Nova Scotia, in a stream that drains a catchment containing 50% bog, the observed annual retention was negligible (Freedman and Clair in press). It should be noted that all of these studies measured retention by the difference between estimated annual inputs from both atmospheric and upland sources and outputs measured in wetland runoff. Since dry deposition is normally not included in the estimates of atmospheric inputs, the retention rates may be underestimated. Also, when comparing sulphate measurements from different studies, one must be certain that the analytical methods used are comparable. Earlier colourimetric methods have been shown to be inaccurate for coloured waters (see Linkage 3.3 below) and thus cannot be compared to measurements based on ion chromatography.

Urban et al. (in press) estimated sulphate retention at several bog sites throughout eastern Canada and the United States, from Minnesota to Newfoundland, by comparing deposition to concentrations in bog waters, corrected for evaporative concentration. They found retention to vary from 60-93% of inputs during summer months, but pointed out that annual

retention may be much less, due to sulphate flushing during high flow periods (see below). Their most significant conclusion, however, was that bog water sulphate concentration increased as deposition increased. This suggests that bog retention of sulphate will not completely mask the effect of deposition on surface water concentrations. Reduced deposition rates will therefore lead to reductions in sulphate contributions from bogs to surface waters. They also found, however, that sulphate concentration increased with increased runoff. This may offer an alternative explanation for the observed gradient, that is not directly related to deposition (see link 2.3). This is clearly a critical uncertainty that needs to be addressed.

Wetlands are not uniformly anoxic at all depths and times. Systems that are connected to oxygenated groundwater sources may in fact have horizons where sulphur is oxidized, rather than reduced, thus generating instead of consuming acidity. Similarly, seasonal changes in hydrology may shift the wetland from a retention mode to a release mode, or at least greatly reduce the retention rates. This prompts the question of to what extent the sulphate retention process is actually a permanent sink for acidity. The fact that all peat deposits contain sulphur suggests at least a partial permanent role.

Kerekes et al. (1982, 1985a, 1985b) and LaZerte and Dillon (1984, 1985) observed pronounced seasonal cycles in the outputs of sulphate from peatlands in Nova Scotia and Ontario respectively. Both found sulphate to be the dominant anion in spring and fall but not in summer. In Ontario, where snowmelt is the most significant hydrological event of the year, sulphate peaked in spring. In Nova Scotia, the maritime climate diminishes the importance of spring snowmelt, and fall storms are more significant. Here the sulphate peak was in the fall. It should be noted, however, these seasonal changes in concentration do not necessarily imply changes in retention rates. At Plastic Lake, sulphate concentrations were highest in spring, but so was retention, in terms of the proportion of the total loadings entering the wetland that did not pass through.

These seasonal cycles are important, as they may effectively eliminate (or at least reduce) the contribution of peatlands as a storage area for sulphate. Measurements of sulphate retention in summer (e.g., Urban et al. in press) may only indicate a temporary storage capability.

Even if annual retention is actually measured, year to year variations in hydrology may override the annual effects.

Finally, where it has been measured, most of the reduced sulphur in the wetland appears to be in organic form (Wieder et al. 1985, Behr 1985, N. Urban, unpub. data). Some of this organic sulphur is exported in reduced form (25% of total S export at Marcell bog: N. Urban, pers. comm.). There is indirect evidence that at least some of this exported reduced S is subsequently oxidized in surface waters (e.g., from the observation that more non-ionic sulphur is present in waters leaving peatlands than in downstream surface waters: E. Gorham, unpubl. data) thus reversing the neutralizing effect of the initial reduction process. Very little is known of the fate of this organic sulphur.

Nitrogen Retention

As mentioned earlier (Hypothesis 1), nitrogen inputs to forested areas in North America, including peatlands, are almost invariably below plant requirements, at least on an annual basis (Johnson and Reuss 1984). Therefore, nitrogen tends to be strongly retained in most catchments, on an annual basis. For example, Bayley et al. (1985) found 99.6% of nitrate added as nitric acid to a fen in northwestern Ontario was retained, while Hemond (1983) observed >90% annual retention of nitrate at Thoreau's Bog and Kerekes et al. (1982) 97.3% annual retention in southwest Nova Scotia. Ammonium also appears to be largely retained by most catchments, so the importance of wetlands (and uplands) as sinks for atmospheric inputs of nitric acid depends on the relative proportions of nitrate versus ammonium in deposition. Uptake of the former consumes acidity while assimilation of the latter produces acidity. Nitrate deposition is generally equal to or greater than ammonium deposition in eastern Canada (Barrie and Sirois 1982).

In contrast to sulphate, nitrogen tends to be strongly retained in uplands as well as wetlands (although sulphate adsorption can be important in some soils - see link 1.6). Thus the importance of wetlands, relative to uplands, as sinks for nitrogen may not be as great as for sulphate. Wetlands are invariably observed to strongly retain N, however, while at some times of the year, and in many catchments, uplands have been observed to release significant amounts of N (link 1.6).

As for sulphur, significant amounts of nitrogen are exported from wetlands in reduced, organic form (30% of inputs at Marcell bog). It is not known what the fate of this organic N is in downstream surface waters, although indirect evidence that it is not oxidized is provided by the observation that the N content of surface water DOC is similar to that leaving bogs. Significant (but generally unmeasured) amounts of reduced nitrogen may also be released from the wetland to the atmosphere, thus providing a permanent sink for acidity. It is largely unknown how significant this quantity might be.

Metals

Peatlands can have a major influence on the amount and chemical form of most of the metals found in surface waters. Three metals for which the role of wetlands is relatively well understood and which are found in relatively high concentrations naturally are aluminum, iron and manganese. This discussion will consider only these three elements.

In fens, aluminum and manganese are primarily derived from upland sources, atmospheric inputs being relatively minor at most locations. For iron, however, the atmosphere can provide an important source. Inputs tend to be lower in the maritimes than in more westerly regions (Ontario, upper midwest states).

There is conflicting evidence as to whether peatlands tend to retain aluminum and manganese. In the Dorset area of Ontario inputs of both elements exceeded outputs (B. LaZerte pers. comm.) while at Marcell Bog aluminum outputs exceeded inputs and manganese was close to being in balance. Coloured surface waters almost invariably have higher aluminum levels than clear waters, suggesting relatively higher outputs from DOC rich peatland waters. Alternatively, this may be due to the higher solubility of organically complexed aluminum. In fact, the observation of higher concentrations of aluminum in coloured maritime lakes than in similarly coloured bog waters (E. Gorham and others, unpubl. data), would suggest that the latter explanation is more likely.

While the extent to which peatlands influence the total supply of aluminum to surface waters is unclear, their influence on the form of aluminum exported is well known. Inorganic aluminum delivered to peat-

lands from upland or atmospheric sources is invariably complexed with the abundant organic anions present in peatland waters. While this may increase the subsequent mobility and solubility of aluminum, it appears to greatly reduce its toxicity to biota (see Hypothesis 4). Thus peatlands probably have a very important influence on the quality, if not the quantity, of aluminum.

Peatlands are invariably sources of iron to surface waters. Iron levels in surface waters are strongly correlated with DOC, suggesting that complexation with organic anions increases the mobility of this element. Iron mobility is also known to be increased by lowered pH and by the presence of a reducing environment, both of which are typical of peatlands as compared to upland areas. DOC and pH also affect the mobility of aluminum and manganese in the same direction as for iron, as does the redox potential for manganese, but not aluminum.

Organic Acid Production

Peatlands are important sources of organic acidity for other surface waters. Most of the acidity derived from peatlands is organic, generated as a result of incomplete oxidation of decomposing organic matter. While upland soils also produce organic acids from litter decomposition, their contribution to surface waters is likely far less than that from wetlands, on a unit area basis, except in special circumstances that prevent water draining upland soils from passing through deeper mineral horizons.

If peatlands are the major source of surface water DOC, then their levels in surface waters should be predictable from knowledge of the proportion of a catchment that comprises peatland. Attempts to test this relationship on Nova Scotia surface waters have met with varied success (Kessel-Taylor 1985, E. Gorham pers. comm.). These analyses have not tended to discriminate among wetland types; little is known about the relative contributions of DOC from different types of wetlands.

Ion Exchange and Assimilation

Peatlands, and especially Sphagnum, also have powerful ion assimilation and exchange capabilities (Clymo 1963). Uptake of anions will tend to reduce acidity while uptake of cations provides a source of acidity.

As for soils, the ability of peatlands to exchange protons for basic cations depends strongly on base saturation and solution pH (Clymo 1983). The ratio of protons to base cations in atmospheric deposition will also influence whether the systems produces or consumes acidity.

Gjessing and Johannessen (1976) showed that metal cations in atmospheric precipitation can be exchanged for protons in humic waters or peatlands, thus providing a source of acidity. This process is not unlike the "salt effect" described earlier, and implies that atmospheric deposition need not be acidic to generate acidic runoff. Examination of coastal peatlands with large sea-spray inputs, however, has revealed no discernable evidence of this effect in these systems (N. Urban and E. Gorham, unpubl. data).

In conclusion, while much research is underway that will continue to improve our quantitative understanding of these processes at specific, intensively studied sites, our knowledge lacks generality. Perhaps the greatest research need at present is to conduct surveys of a variety of wetland types, across regions, with the purpose of establishing the representativeness of the intensively studied sites. The primary information gathered by these surveys would be estimates of element exports in at least two seasons.

Other research needs related to Linkage 2.5 include:

- peat cores across a gradient of atmospheric loading rates and water retention times to look at element (especially S) storage in peat profiles;
- sulphate budgets on calibrated fens and bogs contrasting in loading rates and water retention times;
- investigations of the fates of organic N and S exported from wetlands;
- estimates of the exports of elements (especially N) from wetlands to the atmosphere;
- further development and testing of empirical models to predict DOC, aluminum and aluminum speciation, on a regional scale; and
- investigations of the long term effects of N fertilization on wetlands.

HYPOTHESIS 3: THE AMOUNT AND COMPOSITION OF ORGANIC MATTER AND MINERAL ACIDITY IN SURFACE WATERS DETERMINE pH AND THE SPECIATION AND SOLUBILITY OF ALUMINUM.

Linkages:

3.1 Seasonal and episodic hydrological changes influence runoff and surface water chemistry.

3.2 The character of organic matter present in a water body impacts on metal chelation and acidic strength.

3.3 The concentration of H^+ associated with organic anions can be determined from knowledge of DOC levels and pH.

3.4 Higher levels of DOC add additional buffering capacity to surface water, at a given pH.

3.5 Decreases in pH due to mineral acidity will reduce binding of aluminum by DOC.

3.6 The chelation of aluminum by organic matter will increase aluminum solubility over that at the same pH but with lower DOC levels.

3.7 Several processes occur within lakes and streams that change both the character and amount of DOC.

Discussion

As discussed earlier, the contribution of hydrogen ions associated with organic anions to the acidity of surface waters, including bog waters, lakes and streams, is highly variable. In some systems it may contribute significantly to the acidity present (Kerekes 1977, Rosenqvist 1978, Glover and Webb 1979, Hemond 1980, Johnson 1981, Krug and Frink 1983, Beck et al. 1974, Driscoll and Newton in press, Kerekes et al. 1985a, Underwood et al. 1985, Glass et al. in press). In other cases and on a regional scale mineral acidity related to sulphates, nitrates or aluminum may predominate (Haines and Akielaszek 1983, Driscoll and Schafran 1984, LaZerte and Dillon 1984, Jefferies et al. in press). The main source of H^+ varies considerably depending on watershed characteristics and hydrology as discussed in Hypotheses 1 and 2. Hypothesis 3 is concerned, not with surveying the relative contributions of mineral and organic acidity in different systems, but rather with their interactions and differential effects on other system parameters in open waters. This allows an evaluation of the consequences of additional pH reductions resulting from acidic deposition on a system which may naturally have a low pH. Interactions between mineral acidity, organic acidity and metals may have important biological implications, as discussed in Hypothesis 4.

Three general factors are considered here:

1. the importance of characterization of the composition of DOC (links 3.2 -3.3);
2. the effect of DOC on aluminum speciation and pH (links 3.4-3.6); and
3. processes in watersheds and lakes and streams which alter the amount and composition of DOC in surface waters (links 3.1 and 3.7).

The input levels of the various ions and DOC in open waters are assumed to be determined primarily by watershed processes. This hypothesis discusses how these inputs interact in surface waters. This will allow prediction of the value of water quality parameters which are important when evaluating effects on aquatic biota.

Linkage 3.1 SEASONAL AND EPISODIC HYDROLOGICAL CHANGES INFLUENCE SURFACE WATER CHEMISTRY.

This Linkage has been well established for many systems in the investigation of snowmelt and storm events that are commonly associated with a decrease in pH and elevated aluminum in surface waters (Marmorek et al. 1984). It is considered here in the context of systems with a high concentration of organic anions. Many workers have noted seasonal cycles in the contributions of mineral anions (SO_4^{2-},NO_3^-) versus organic anions (A^-) in ion balances of lakes and streams draining peaty watersheds (Kerekes et al. 1982, LaZerte and Dillon 1984, Visser 1984, Clair 1985, Kerekes et al. 1985a, Kerekes et al. 1985b, Kessel-Taylor 1985, Clair and Freedman in press). The sulphate ion predominates in the late fall and spring and the organic anions dominate in the drier summer months. In the work of Kerekes et al. (1985a) iron and aluminum exhibited the same pattern as A^-. The hydrogen ion, although always present in higher concentrations than SO_4^{2-}, shows the same seasonal patterns as SO_4^{2-}. This seasonal variation was not observed in lakes, ponds and streams in Acadia National Park, Maine where colour ranged from approximately 15-25 Pt-Co units. In these systems the SO_4^{2-} concentration remained relatively constant throughout the spring and summer (Kahl et al. 1985). These findings suggest that the relative contributions of organic and inorganic acidity to the total acidity vary seasonally.

The main source of the sulphate in the fall is likely to be from

heavy fall rains. Further investigation is required, however, into the sources in the spring. It is important to determine whether the main source is flushing of material accumulated in the snowpack as a result of anthropogenic deposition or from peatland drainage (Clymo 1984, Singh 1984).

The seasonal patterns are more marked in headwater streams. The responses are damped in outlet streams due to retention in the lake (J. Underwood pers. comm., Kerekes et al. 1985b). Lake and stream order may be important in these seasonal variations. This factor requires further investigation.

Although pH was found to be related to DOC spatially across a range of different highly coloured water bodies, there was no correlation between pH and DOC in a single water body throughout the year (Clair and Freedman in press; Kessel-Taylor 1985, Kerekes et al. 1985a). This may result from a change in the characteristics of the DOC through time as discussed in Linkage 3.2. Further research into the relationship between temporal changes in the type of DOC present and pH was recommended. A statistically significant correlation was found between pH and SO_4^{--} through time suggesting mineral acidity may be an important factor in variations in pH within a single basin (Clair and Freedman in press).

The principal research need for this Linkage is that both the seasonal variation in organic versus inorganic anion concentrations and temporal pH variation should be investigated in terms of the relative contribution of drainage from uplands and wetlands in the watershed.

Linkage 3.2 THE CHARACTER OF ORGANIC MATTER PRESENT IN A WATER BODY IMPACTS ON METAL CHELATION AND ACIDIC STRENGTH.

Frequently, dissolved organic matter is characterized by a total DOC measurement only. A more detailed characterization may be required, however, since the associations between organic matter and aluminum are a function of the properties of the organic matter present.

The contribution of H^+ from organic matter depends on the number and type of functional groups present as well as the degree to which these functional groups are dissociated. There are several techniques which have been used to characterize organic matter. The acidic functional

groups present are primarily the carboxylic and phenolic groups (Perdue 1985). A complex model using statistical thermodynamics to estimate a continuous distribution of both carboxylic and weakly acidic binding sites has been developed by Perdue and co-workers to describe the extent of proton binding across a pH range (Perdue et al. 1980, Perdue et al. 1984, Perdue 1985). This approach may provide an accurate description of the acidic strength of organic matter present.

Another method uses potentiometric titrations to determine the pK's for the main acidic groupings of colloidal substances including humic materials (Arp 1983b, Arp 1983c). With the titration curve, consideration for surface potential and the number of pK's are input into a computer program which calculates the equivalent concentrations and values for the pK's which best fit the titration curve. The final number of pK's is the minimum number after which an additional pK does not result in an improved fit. This method has been shown to be independent of concentration of organic matter. It also allows one to interpret the hysteresis in titration curves which may occur due to molecular rearrangements including autoxidation at high pH. It does require standardization of sampling and analysis technique since natural substances do not yield method-independent titration curves.

Another approach discussed is classification by fractionation. A method has been developed by the United States Geological Survey (Leenheer and Huffman 1976, Leenheer and Huffman 1979, Leenheer 1981). This method was used to characterize the DOC and to evaluate the acidic functional group content in Thoreau's Bog and in watersheds in Adirondack Park (Cronan and Aiken 1985, McKnight et al. 1985). At present there is work in progress in southwestern Nova Scotia applying a slight modification of this technique to classify dissolved organic matter into seven general components (Rick Bourbonniere pers. comm.):

1. humic;
2. fulvic hydrophobic acidic;
3. fulvic hydrophobic basic;
4. fulvic hydrophobic neutral;
5. fulvic hydrophilic acidic;
6. fulvic hydrophilic basic; and

7. fulvic hydrophilic neutral.

The fractions are operationally defined based upon adsorption by non-ionic and ionic exchange resins. The study includes bog drainage waters (approximately 75 per cent of sites) and streams and lakes in Kejimkujik National Park (approximately 25 per cent of sites) with DOC's ranging from 5-71 mg/l . Preliminary results show that the fulvic hydrophilic acid fraction ranges from 0-36 per cent of the DOC averaging about 15 per cent. This fraction represents the "strong" acidity associated with DOC. It is frequently neglected when estimating the concentration of A^- from DOC but is clearly present in significant proportions.

The seasonal variability of DOC characterization is also being studied and preliminary results indicate a great deal of variation in the make-up of the organic matter present (R. Bourbonniere pers. comm.).

There are several possible future applications of both the fractionation and titration techniques. For example, potentiometric titrations on the various fractions after separation could be used to measure the pK's of each fraction and thus determine which fractions are strongly or weakly acidic.

Aluminum associations with DOC may also be a function of the composition of the DOC. A method analagous to the potentiometric titrations could also be used to evaluate aluminum chelation at different pH's. This could possibly be related to the pK's of the DOC. Finally, the fractionation technique could be used to determine the fraction in which metal interactions were the most important.

Another method of classifying organic matter is by molecular weight. Visser (1982a) found that the surface binding of aquatic humus increased with rising molecular weight. This agrees with the work of Davis and Gloor (1981) who found that organic compounds with molecular weights greater than 1000 form strong surface complexes with aluminum oxide. The mechanism of adsorption is related to complexes formed between the alumina surface and carboxylic and phenolic functional groups of natural organic matter. Low molecular weight organic compound (less than 1000) were weakly surface sorbed. Surface complexation with aluminum oxide precipitates much of the higher molecular weight organic material out of solution resulting in a shift in the molecular weight distribution of

dissolved organic material. Since the intermediate molecular weight fraction (1000-3000) forms the strongest complexes with trace metals, it may also be important to consider aluminum chelation with particulate as well as dissolved organic carbon.

Davis and Gloor (1981) noted the seasonal variation in the molecular size distribution of organic matter present in Lake Greinfensee, Switzerland and related this to changes in algal productivity. It would be of interest to investigate any relationship between the changes in the molecular weight of the organic matter present in a system and the seasonal variation of aluminum.

There are methodological concerns associated with determination of the molecular weight distribution of DOC. Aiken (1984) discusses problems involved with the ultrafiltration technique frequently used for determining the molecular weight of fulvic and humic acids. Interactions between ultrafiltration membranes and the solute as well as imprecise molecular weight cut-offs may result in incorrect determination of molecular weight distribution.

The activity of organic matter of aquatic origin has been found to depend also on its origin, functional group content and state of humification (Visser 1982b). The importance of these factors suggests that commercial humic substances or those derived from sources other than aquatic systems may be poor models of DOC behaviour in surface waters since the molecular weight and functional group distribution may be very different (Davis and Gloor 1981).

There is evidence to suggest that the characteristics of DOC vary both spatially and temporally (Laegreid et al. 1983, Cronan and Aiken 1985, McKnight et al. 1985, Rick Bourbonniere pers. comm.). Further, it has been shown that these characteristics can influence both the organic acidity associated with DOC and interactions with metals. Future research in several areas is needed to elucidate the importance of DOC characterization. The intra- and interregional variation in characteristics should be studied and related to watershed characteristics. These studies should include high pH, high DOC systems present in Cape Breton and Newfoundland since the organic matter in these water bodies appears to contribute less acidic strength than those in southwestern Nova

Scotia. Similarly, seasonal variation should be examined to ascertain whether there are seasonal patterns and if so, how these patterns relate to seasonal variation in other water quality parameters as discussed in Linkage 3.1.

The work on methodologies for DOC characterization by both potentiometric titration and fractionation should continue. In addition, the relationship between colour, pH and DOC should be further investigated to determine if spectrophotometric absorbance could be used for characterization. In a given water body, colour and pH and colour and DOC are highly correlated. The relationship between these variables should be investigated on a regional scale. If a relationship between absorbance and acidic strength or the potential for metal chelation could be found, it would provide an extremely simple technique for characterization.

Finally, research is required to determine the effect of changes in DOC composition on aluminum association. Once an appropriate methodology for characterizing organic matter has been chosen, the change in stability constants should be quantified with respect to changes in character as measured by this technique.

Linkage 3.3 THE CONCENTRATION OF H^+ ASSOCIATED WITH ORGANIC ANIONS CAN BE DETERMINED FROM KNOWLEDGE OF DOC LEVELS AND pH.

As was discussed in the previous Linkage, methodological considerations are very important when evaluating organic acidity. There are several variables frequently used as a surrogate measure of organic acidity including DOC, DOM, TOC and colour. The actual reduction of pH associated with organic matter is given by the concentration of hydrogen ions which have been contributed from organic matter due to the presence of acidic functional groups, primarily the carboxylic and phenolic functional groups (Perdue 1985). Frequently, however, the complex organic acid is considered as a simplified acid, HA, where A^- represents the associated organic anion.

In the past, organic anion concentrations have been estimated from the difference between total measured cation and anion equivalent concentrations in water. It has been shown that the methyl thymol blue (MTB) method frequently used for SO_4^{2-} analysis overestimated the true SO_4^{2-} in

coloured waters (Cronan 1979, Kerekes and Pollock 1983, Underwood et al. 1983, Kerekes et al. 1984). This has led in the past to underestimates of A^-.

This Linkage suggests that characterization of DOC is not required to determine the acidity associated with organic matter but that organic acids may be considered as HA and that the concentration of A^- can be determined from DOC and pH. One model which has been developed to determine A^- as a function of DOC and pH is that of Oliver et al. (1983). It involves two key assumptions. The first is that the carboxyl group is the main acidic functional group (phenolics are not considered) and that there is little variation in the carboxyl content of humic matter from different regions. This is based on a set of 19 samples from diverse locations across Canada and the United States which show an average carboxyl content of 10.5 ueq/mg C with little variation between samples. Other workers however, have cited significantly different acidic functional group contents (Henriksen and Seip 1980, Cronan and Aiken 1985, McKnight et al. 1985). The range of acidic functional group content in the study of Oliver et al. (1983) was 8.3 - 13.4 ueq COOH/mg C for fulvic acids and 5.1 - 9.9 ueq COOH/mg C for humic acids. Cronan and Aiken (1985) report a range of 6.4 - 8.3 ueq COOH/mg C for soil leachates. The work of McKnight et al. (1985) highlights the difference between the hydrophobic and hydrophilic fractions. They found the average carboxyl group content of the hydrophobic fraction was 10.1 ueq COOH/mg C and that of the hydrophilic fraction was 13.2 ueq COOH/mg C. Some of these differences may be due to the methodologies employed. Oliver et al. (1983) isolate and purify the fulvic and humic acid fraction from the DOC and titrate to pH 7 only. Their isolation technique recovers 40-75 per cent of the organic material and excludes the low molecular weight organic acids which may be a source of strong acidity (the hydrophilic acids in the fractionation procedure).

The relationship between pH and the degree of dissociation of the humic substances used by Oliver et al. (1983) is based on a potentiometric titration of two fulvic acid samples. Other studies are cited which show similar dissociation relationships. On the other hand, a similar titration on all fractions of DOC shows that hydrophilic acids may behave differently (McKnight et al. 1985).

Although the relationship between A^- and DOC and pH has been developed on a limited data set, it has resulted in accurate ion balances in systems which previously exhibited an anion deficit (Oliver et al. 1983). The model has been applied to lakes and streams in the U.S. National Surface Water Survey. The results of the empirical model were compared to direct titration of organic acidity and produced a good fit on average (J. Kramer pers. comm.).

A similar approach to that of Oliver et al. (1983) is taken by Driscoll and Bisogni (1984) who have developed a simple monoprotic proton dissociation constant model (pK =4.41) for Adirondack waters. The same model is applied by Driscoll and Schafran (1984) to a different lake in the Adirondacks. The total organic carbon proton dissociation/association sites were correlated to DOC (Driscoll and Schafran 1984) and TOC (Driscoll and Bisogni 1984).

In a discussion of this and other similar models, Wiltshire (1983) points out that the purified or isolated humic substances used in these studies may behave differently than natural organic acids due to possible denaturation during isolation and the effects of metal complexation.

The model of Oliver et al. (1983) appears to provide a good empirical relationship to determine A^-. Caution is required when utilizing this relationship, however, since the main evidence for its validity was achievement of accurate ion balances in certain systems. Continued testing of the relationship of Oliver et al. (1983) is strongly recommended. An estimate of the regional and temporal variability in the accuracy of the model predictions is required.

One key question in considering the water chemistry of surface waters high in DOC, is whether DOC is a sufficient measurement of organic matter or if further characterization is required. Clearly if no measurement beyond DOC is required analysis is greatly simplified. Further testing and refinement of the empirical relationship of Oliver et al. (1983) can help to answer this question with respect to the acidic contribution of organic matter. In many cases, sufficient data for this analysis may already be available in existing data sets.

Linkage 3.4 HIGHER LEVELS OF DOC ADD ADDITIONAL BUFFERING CAPACITY TO SURFACE WATER, AT A GIVEN pH.

The effect of DOC on the pH control of a system has been shown to be important when considering sensitivity to additional anthropogenic acidity (Wiltshire and Machell 1981). The magnitude of the buffering effect of the organic acid-base conjugate pair is a function of the DOC concentration and the system pH.

Wilson (1979) mathematically describes the buffer intensity of a system with assumed levels of DOC and DIC (dissolved inorganic carbon) and concludes that DOC is a poor buffer at average surface water concentrations of 1-4 mg/l. However, at a higher concentration (10 mg/l), which is considered representative of dystrophic waters, in a pH range of 4-5, the buffering capacity of organic acids rivals that of carbonate systems.

Wiltshire (1983) performed similar calculations and found buffering from DOC to have a significant effect in the range where bicarbonate buffering is at a minimum (pH 4.5 - 5.5). He points out that when comparing the buffering capacity of systems with high and low levels of DOC, differences in pH must be taken into account. DOC will reduce pH and may reduce total buffering capacity at certain concentrations by shifting the system to a pH range where it is more sensitive to acidic inputs due simply to reduced carbonate buffering. Indeed, all buffers present in the system must be considered when evaluating the effects of a pH change due to additional DOC.

Aluminum is another source of weak acidity and also provides some buffering. It generally has a higher buffering capacity than DOC. In Norwegian waters, however, DOC is typically present in concentrations 20 - 200 times those of aluminum and thus provides a greater total buffer (Johannessen 1980). In the pH range of 5.0 - 5.5, natural organic matter masks aluminum buffering, perhaps through complexation reactions. In Adirondack waters, Driscoll and Bisogni (1984) conclude that aluminum buffering controls the lower limit of the observed pH values. Since this limit is quite low (pH of approximately 4.0), the complexation of aluminum by DOC would be reduced and aluminum would therefore have a higher buffering intensity.

Again the question of DOC characterization must be considered. The buffering capacity and pH range in which it is effective depends on the

number and type of functional groups present. Therefore, studies of regional and temporal variability in the composition of DOC should include an investigation of the associated changes in buffering capacity.

Linkage 3.5 DECREASES IN pH DUE TO MINERAL ACIDITY WILL REDUCE BINDING OF ALUMINUM BY DOC.

The toxicity of aluminum to aquatic biota may be greatly reduced through binding with organic matter as discussed in Hypothesis 4. It is therefore important to consider factors which may affect the relative proportions of free and bound aluminum. The speciation of aluminum is determined by the pH of the solution and the abundance of ligands, particularly fluoride, sulphate and organic ligands, available to complex aluminum ions. In Linkage 3.2 the effects of changes in the amount and character of the organic anion were discussed; in this Linkage the effect of changes in pH is considered. If, in addition to the increased solubility of aluminum at decreased pH (Hall et al. 1980, Driscoll and Bisogni 1984), the proportion of soluble aluminum which is chelated by organic anions is reduced, a significant increase in toxicity would be expected.

Thermodynamic calculations (Campbell et al. 1985) predict that in the pH range 7.0 - 4.0, a reduction in pH will result in a reduction of the degree of complexation of aluminum. Schnitzer (1980) predicts the same relationship based on the decrease of the stability constant for metal-fulvic acid complexes with decreasing pH. In a field study in the Adirondacks, however, Driscoll (1980) found the concentration of organic monomeric aluminum to be independent of pH where TOC ranged from 4-10 mg/l.

An additional interaction between organic matter and aluminum is the adsorption of organic matter on aluminum oxides. Davis (1982) found that adsorption was at a maximum at pH 5 and decreased as the pH either increased or decreased from this value. The complexes formed between organic matter and aluminum oxides commonly precipitate out of solution reducing DOC levels in the water. A reduction of pH below 5 would result in reduced adsorption and therefore, increased DOC available for aluminum binding. The net effect of increases in both DOC and H^+ on aluminum binding, however, cannot be determined from this study.

The kinetics of speciation changes have been studied and preliminary results suggest that pH induced changes occur rapidly enough to respond to short term fluctuations in pH (Campbell et al. 1985, LaZerte 1985). This implies that changes in aluminum speciation can be expected in response to changes in pH or DOC related to storm and snowmelt flow events. It was recommended at the workshop that research continue on the kinetics of changes in aluminum speciation. If changes do not occur rapidly, there may be periods in which free aluminum is present during episodic events in systems in which virtually all the aluminum is bound by organic matter at other times.

In systems with high DOC such as those in eastern Canada, essentially all the aluminum is probably bound by organic matter. Research into the degree of saturation of organic matter by aluminum is required in surface waters exhibiting a range of DOC concentrations. Work of this type is in progress at the University of Maine (S. Kahl, pers. comm.) however, no data are presently available. This work could be related to the characterization of organic matter with respect to aluminum associations recommended in Linkage 3.2.

While discussing aluminum speciation, the need for consistent analysis techniques to allow comparability between studies was emphasized. In relation to this, the empirical relationship developed by LaZerte (1984) should be tested on highly organic waters. This relationship predicts the amount of free versus bound aluminum based on total monomeric aluminum, pH and TOC. If an accurate relationship of this kind was found to apply interregionally (including coloured waters) it would imply that characterization of organic matter with respect to aluminum interactions is not required for evaluation of free aluminum levels.

Linkage 3.6 THE CHELATION OF ALUMINUM BY ORGANIC MATTER WILL INCREASE ALUMINUM SOLUBILITY OVER THAT AT THE SAME pH BUT WITH LOWER DOC LEVELS.

The proportion of total aluminum which is present in dissolved forms may have significant biological effects; therefore it is important to consider effects of DOC on solubility. Soluble monomeric aluminum may be in inorganic form as Al^{+3}, $Al(OH)_x^{+(3-x)}$, $Al\ F_x^{+(3-x)}$, and $Al(SO_4)_x^{+(3-2x)}$ or complexed with DOC (Driscoll 1980). The types of

interactions with organic matter which influence aluminum speciation have been described as ion exchange, surface adsorption , chelation and coagulation (Schnitzer and Khan 1972). Reuter and Perdue (1977) found the stability of metal-humic complexes in natural waters higher than those of the corresponding inorganic metal complexes.

Perdue et al. (1976) reported a strong correlation between dissolved organic matter and the sum of the concentrations of dissolved aluminum plus iron. They suggest that the two factors involved in the competition of metals for complexing sites are the stability constants of the metal-organic acid complex and the relative abundance of a given metal. Any increase in total aluminum would, therefore, increase the number of complexing sites occupied by aluminum.

In a study on lakes and streams in the Adirondack region, Driscoll (1980) found, using thermodynamic equilibrium calculations, that organically complexed aluminum was generally the predominant soluble form. The inorganic soluble complexes were present in lower concentrations. Total soluble aluminum concentration was found to be significantly correlated with total organic carbon measurements.

Both Driscoll et al. (1980) and LaZerte (1984) found that the organically complexed form of aluminum was highest during summer periods. Kerekes et al. (1985a) found changes in aluminum concentration corresponded to the seasonal patterns of organic anions. Conversely, Haines and Akielaszek (1984) found a peak in total aluminum during high discharge when sulphate and nitrate peaked. They also found, however, a positive correlation between aluminum and organic anion concentration in nine streams in New England.

Linkage 3.7 PROCESSES WHICH OCCUR IN LAKES AND STREAMS CHANGE DOC LEVELS AND COMPOSITION.

Several processes may occur during the retention period in surface waters leading to changes in the amount and composition of DOC present in a system. Microbial degradation results in the breakdown of large organic molecules to form smaller fragments (Wetzel 1975). This will result in an increase in the concentration of low molecular weight, strong organic acids as well as CO_2 production.

The process of humification of organic matter results in the formation of larger more refractory organic molecules which may precipitate out of solution. This also acts to change the acidic functional group composition of DOC, reducing the concentration of H^+ associated with the organic matter.

A final process which may alter DOC composition in surface waters is photooxidation (Driscoll et al. 1985). The significance of photooxidation is not well understood and it was felt that further investigation of its importance was required.

Research relating to these processes is needed on two levels. The first is laboratory studies into the changes in composition of DOC resulting from these reactions and the kinetics associated with these changes. This work should include investigation of changes in pK's and metal stability constants. The kinetic studies could be related to surface water residence time to allow prediction of the extent to which these reactions would proceed.

The second level of study would involve field measurements on whole catchments. The inflows and outflows of DOC for a lake should be compared to the levels in a lake to allow calculation of a DOC budget. This would provide an examination of the net effect of processes occurring in a lake to determine if inflows and outflows were balanced by sedimentation of organic matter. This work would be difficult since there may be many sources of DOC into a lake in addition to major inflowing streams. The data for a DOC budget may exist for calibrated watersheds. Such existing data should be examined since sufficient information may already be available for this type of study.

Decreased pH due to mineral acidity may alter the processes which act on organic matter. Reductions in microbial activity corresponding to reduced pH due to acidic deposition have been documented (Traaen 1980, Rao and Dutka 1983, Allard and Moreau 1985). This change in the rate of degradation of DOC may result in a shift of the composition of DOC present in a system. This may in turn result in a change in metal binding or acidity associated with organic matter.

Changes in water clarity have also been associated with acidic deposition. Increased light penetration would result in increased photooxida-

tion of organic matter.

Humic substances in soil and peatland water are not the only source of organic matter to surface waters. There may be autochthonous production from autolysis of cytoplasmic cellular contents from algae and macrophytes and from secretions from actively growing algae and plants. Although secreted compounds are generally rapidly assimilated, a proportion of the degradation products from algae and macrophytes are resistant to decomposition and analogous to humic substances from terrestrial environments (Wetzel 1975). The relative proportions of allochthonous and autochthonous organic matter vary depending on watershed inputs of humic substances, productivity in the surface waters and bacterial activity. Visser (1982a) found aquatic humic material more surface active than that of terrestrial origin and also found that acid groups play a more important role in surface activities of fulvic acids of aquatic origin when compared to those of terrestrial origin.

In general, autochthonous production of dissolved organic matter in streams is very much less than allochthonous inputs and the organic matter present is similar to fulvic acids present in soil water (Reuter and Perdue 1977, Visser 1982a). In lakes, however, autochthonous production may be more significant depending on the percent littoral area and the phytoplankton biomass in the system. Effler et al. (in press) found in Dart Lake in the Adirondacks, autochthonous production of DOC was low due to a low standing crop of phytoplankton. Driscoll and Bisogni (1984) found a greater quantity of aluminum complexing organic carbon in lake water than in stream water in the Moose Lake watershed in the Adirondacks; they attribute this to autochthonous organic matter production in the lake. Nevertheless, while autochthonous production may contribute significantly to the total DOC pool in clear waters, in coloured waters it is generally far less important than the high fluxes of DOC from the watershed.

HYPOTHESIS 4: THE MORTALITY OF BIOTA DUE TO SURFACE WATER ACIDIFICATION DEPENDS DIRECTLY ON THE CONCENTRATIONS AND CHEMICAL FORM OF ACIDS, ALUMINUM AND BASE CATIONS, AND THE SPECIES, LIFE HISTORY STAGE AND BEHAVIOUR OF THE BIOTA OF CONCERN, AND INDIRECTLY ON RELATED EFFECTS ON OTHER BIOTA.

Linkages:

4.1 The mortality of biota is influenced by:
- a) the concentrations of mineral acidity;
- b) the concentrations of organic acidity;
- c) the concentrations of metals, primarily aluminum; and
- d) the ameliorating effects of base cations.

4.2 The growth, reproduction and behaviour of biota is influenced by:
- a) the concentrations of mineral acidity;
- b) the concentrations of organic acidity;
- c) the concentrations of metals, primarily aluminum; and
- d) the ameliorating effects of base cations.

4.3 The growth and reproduction of biota is influenced by the mortality of other biota (competitors, predators, or prey) in the system of concern.

4.4 The mortality of biota is influenced by the growth, reproduction, and behaviour of other biota. (competitors, predators, or prey) in the system of concern.

4.5 The species composition of the system of concern is determined by the growth, reproduction, and mortality of its biota.

Discussion

It was the intent of this hypothesis to consider two major issues: the effects of organic acidity on aquatic biota, and the effects of wetland acidification on biota using wetland habitats. Much more scientific effort has been devoted to understanding organic acidity effects on aquatic biota than specifically to the issue of wetland acidification effects. Therefore, most of the discussions below are relevant to the former issue; the latter remains an area of needed research which will be discussed at the end of this section.

Section 2.4 of the report prepared by Marmorek et al. (1984) provides a comprehensive review of laboratory and field studies demonstrating the effects of pH and aluminum on particular fish, amphibian, and insect species. This summary document also provides some references to initial studies examining the ameliorating effects of organic acids and

base cations (Brown 1981, Wright and Snekvik 1978). Rather than repeat this exhaustive review in this discussion, only more recent results on the effects of pH and aluminum on aquatic biota will be examined. As well, the following issues will be addressed more thoroughly:

1. direct toxic effects of organic acids on aquatic biota;
2. interactions between organic acids, pH, and aluminum which may influence the toxicity of surface waters to aquatic biota;
3. food chain effects of acidification; and
4. the responses of organisms living in wetland environments to wetland acidification processes.

There is sufficiently poor information on wetland acidification effects on wetland biota that this was recognized as an item of important and necessary research.

It is important to recognize the value and limitations of particular research strategies. Research on acidification effects can be divided into four major classes:

1. laboratory studies help to define the relationships between acidification variables and biological parameters of concern such as fish growth or survival. They are not able to predict effects on an extensive basis, although they do suggest what relationships should be observed in extensive surveys;
2. field bioassays provide field validation of laboratory bioassay results and often help elucidate the role other environmental variables play in determining biotic responses to acidification;
3. intensive medium scale studies, such as calibrated watersheds, are essentially ecosystem bioassays. They provide insight into how acidic deposition is influenced by physical, chemical, and biological processes to produce acidification of aquatic systems and concomitant effects on biota but results from these types of studies are difficult to extrapolate to other areas; and
4. extensive surveys help to define correlative relationships between biotic parameters of concern and acidification variables. Biological parameters of concern can usually only be measured with gross indices such as presence/absence or annual species diversity. They do not demonstrate cause and effect but can provide strong evidence that acidification processes observed in laboratory or field bioassays occur on an extensive basis.

Biota Utilizing Waters High In Organic Acids

All major classes of aquatic biota inhabit waters high in organic acids, but the species assemblage is often very different than that found in waters low in organic acids.

Many waters which are high in organic acidity do not support fish populations (Blancher unpubl. manus.) because of lack of suitable breeding habitat or high acidity (Rahel and Magnuson 1983). Rahel (1984) found that water bodies surrounded by bog contained little fish fauna at very low pH and contained primarily cyprinids at pH above 5.2. In recent surveys of small peatland pools of northern Ontario, Blancher and McNicol (in prep.) found that some peatland waters at pH 4.8 and above contained primarily cyprinids and sticklebacks while no fish were detected in pools at pH below 4.8. Waterfowl tend to use peatlands and bog areas in the summer only (Brewer 1967). Waterfowl tend to utilize those waters which contain appropriate food items in sufficient quantities for raising young during the spring and summer (Bendell et al. 1983) and are therefore more concentrated in fens and open peatlands with water than strict bogs (Erskine 1977). Amphibians also use waters high in organic acids (Blancher and McNicol in prep.). Freda (1985) states that for breeding in the spring, amphibians utilize temporary forest ponds that may be high in organic matter.

Linkage 4.1 THE MORTALITY OF BIOTA IS INFLUENCED BY THE CONCENTRATIONS OF MINERAL ACIDITY, THE CONCENTRATIONS OF ORGANIC ACIDITY, THE CONCENTRATIONS OF METALS, PRIMARILY ALUMINUM, AND THE AMELIORATING EFFECTS OF BASE CATIONS.

Acidic precipitation has been found to influence many types of aquatic biota (Haines 1981). This review focusses on new information available on particular aquatic biota from studies which have been conducted since the review of Marmorek et al. (1984).

Direct Effects of Organic Acidity

The toxicity of organic acidity to aquatic biota is poorly understood and, indeed, barely researched. Very few studies specifically address the direct effects of organic acids on survival and growth of aquatic biota. Furthermore, it may be difficult to conduct research on

direct effects of organic acidity because of:

1. the specific origin of organic matter, its pathway through the watershed, and the influence of origin and pathway on the mixture of compounds which normally comprise organic acidity; and
2. confounding factors such as aluminum complexation (see below).

Some research findings do exist, however. Recent studies on toxic effects of acidic environments on amphibians hint at the importance of organic acidity. Clark and Hall (1985) found that hatch success of three amphibian species declined as DOC levels increased. Dunson and Connell (1982) and Freda and Dunson (in press) report similar findings. The factors causing these observations are not known and detrimental influences other than those related to acidity may be operating. Also, very preliminary work by Freda (pers. comm.) showed that some amphibian species suffered greater mortality in high organic waters than low organic waters with similar pH and other conditions. Karns (1983, cited in Freda 1985) found amphibian responses to increasing levels of DOC and Peterson (pers. comm.) has observed DOC-related effects on fish in extreme situations of very high DOC.

It may be inappropriate to put a great deal of effort into elucidating the direct effects of organic acidity on biota because current evidence indicates that the dominant role of organic acidity is to ameliorate acidification through the binding of metals, particularly aluminum (see below).

Effects of Organic Acidity on Aquatic Productivity

Organic acidity does influence aquatic systems in ways other than direct or interactive acidic effects. For example, organic acids strongly attenuate light, causing reduced euphotic depth and consequent limits on areal primary production (Kerekes 1975). Kerekes *et al.* (in press) found that bog drainages in brownwater lakes may have a greater supply of dissolved total phosphorus (although a large proportion of it is not available biologically) and allochthonous organic particulate matter causing greater primary production at optimum light and greater zooplankton productivity.

Direct Effects Of pH

The results of studies documented in the review of pH effects on biota in Marmorek et al. (1984) are generally confirmed by recent field bioassays (Freda and Dunson in press, Lacroix 1985a and b, Lacroix et al. 1985) and are partially supported by field surveys (Underwood et al. 1985, Glooschenko et al. 1985 and Matuszek and Wales 1985), although there may be confounding factors, such as aluminum or other metals, acting to affect organisms and reduce populations or species diversity in some of these studies.

Recent studies provide further evidence of the direct effects of low pH. For example, Freeman et al. (1983) and Freeman and Sangalang (1985) found decreased blood sex hormone levels in caged fish held in an acidic river (pH=4.7) than levels in fish held in a less acidic system (pH=5.6). A historical analysis of Atlantic salmon angling success in Nova Scotia (Watt et al. 1983) indicates that angling success has decreased in river systems with declining pH while angling success has remained comparatively constant in systems with more constant pH levels. Finally, Bendell and McNicol (in prep. a) found that small northern Ontario lakes with a depauperate lithophilous cyprinid fauna were lower in pH than lakes with a normal lithophilous cyprinid fauna.

Base Cation Effects

Evidence is accumulating that base cations can have a major influence on the direct toxic effects of pH on aquatic biota. Peterson (pers. comm.) has found that Atlantic salmon fry can tolerate very low pH with sufficient Ca^{2+} levels, but that they can not survive moderate levels (pH=6.5) with low Ca^{2+}. These preliminary findings are supported by the results of work done by Holtze and Hutchinson (1985) on lake trout and brook trout, Tietge et al. (1985) on brook trout, and Ingersoll et al. (1985) on brook trout. Similarly, Dale et al. (1985), Freda (1985) and Freda and Dunson (in press) report that sufficient levels of calcium, magnesium, and sodium may reduce the deleterious effects of low pH on amphibian hatching success and that these effects are species specific. Bendell and McNicol (in prep. a) found that lakes they studied which were depauperate of lithophilous cyprinids were lower in calcium than lakes which had normal assemblages of these species. The findings of Kessel-

Taylor (1985), that many of the base cations are positively correlated with percentage wetland in ten Nova Scotia watersheds suggests that wetlands may be able to provide base cations to waters and help ameliorate direct pH effects on aquatic biota in these waters. Lacroix (1985a,b) and Lacroix et al. (1985) found that lethal and sublethal effects on Atlantic salmon were probably related to effects of H^+ at low Ca^{2+} concentrations. He found the relationship between Atlantic salmon mortality and pH in the field to be shifted to higher pH levels than in laboratory studies, apparently because of the relatively low Ca^{2+} levels in the acidic rivers of Nova Scotia.

Aluminum

Research conducted into aluminum toxicity on aquatic biota since the review of Marmorek et al. (1984) has focussed on expanding the scope of biota studied (Kramer and Hummel 1985, Freda and Dunson in press) and improving the understanding of the mechanisms of aluminum toxicity (Hutcheson and Strong 1982; Hutcheson and Odense 1984; Lee and Harvey 1985). In a survey of a number of Ontario lakes, Bendell et al. (1983) found that fishless lakes had significantly higher aluminum concentrations than lakes containing fish populations.

Interactions Between H^+, Aluminum, and Organic Acids

The hypothesis of interaction between H^+, aluminum, and organic acids, which is supported by some experimental evidence, is that organic acids decrease the toxicity of the aquatic environment because aluminum is complexed by the acids (Baker and Schofield 1980). These results are supported by Vaughan et al. (1982) and Howell (in prep.) who found that diatoms preserved in the sediments of lakes high in organic acids were largely composed of acid-intolerant species. This could be caused by adaptation of populations of those species to a chronically low pH environment or to the reduction in metal toxicity by the presence of organic acids. Similar results were found by Janzen (1974) in tropical systems. Huttunen and Merilainen (1983) and Davis et al. (1985) observed similar differences in diatom assemblages in humic waters than in clear waters but did not indicate they were dominated by acid-tolerant species. Kerekes (1982) found that the relationship between fish presence/absence and pH in Kejimkujik National Park, an area in which most river systems

are highly coloured, was at approximately 0.4 pH unit lower than similar relationships developed elsewhere for clearwater lakes. Finally, Lacroix (1985b) found that aluminum in his systems was not a major mortality factor to Atlantic salmon because most of it had been bound up by the high levels of organic acids in his Nova Scotia river systems. It is generally felt that this was likely to be true for many of the acidic systems of Atlantic Canada, although the relationship between organic carbon levels and the ability of organic compounds to bind the aluminum present in these systems is not yet well understood. The ability of organic acids to bind aluminum and remove or greatly reduce its toxicity to biota could vary with the composition of the organic acidity, the levels of aluminum in the system, and the pH of the system.

A major, and yet unanswered question, relating to the interactive effects of organic acidity, mineral acidity, and aluminum on biota is whether, in terms of aluminum toxicity to aquatic biota, the composition and characteristics of organic acidity are important in determining its ability to bind aluminum. This has important implications for attempts to assess regional effects of acidification on aquatic biota in which DOC is currently used as the indicator of organic acidity. A major research need is to find out if, in fact, DOC is a reliable indicator of the aluminum binding capacity of the organic acids present in surface waters.

Life History Stage Differences

Different life stages of the same species have differential susceptibility to effects of acidic precipitation. It is agreed that older life history stages of aquatic biota are, in general, less vulnerable to mortality effects. This is supported by recent work on amphibians by Freda (1985) and Freda and Dunson (in press) who found lethal pH levels to be lower for larval than embryo stages. This general relationship between decreasing vulnerability and increasing age is not always true however. For example, Daye and Garside (1979) found that Atlantic salmon alevins were more vulnerable than eggs to low pH. Similarly, Ingersoll et al. (1985) found that yolk sac and swim-up brook trout fry were more vulnerable to acidic influences than eyed eggs. These differences are apparently solely due to the chorion and perivitelline fluid. "Eyed" eggs are just as vulnerable as hatched alevins if these are removed

(Peterson, pers. comm.). Lacroix (1985b) found that Atlantic salmon smolts are more sensitive to sublethal effects of low pH than parr, although young parr (0+ age class) are more sensitive than older parr. However, the lethal effects of low pH are greater for the early fry stage of Atlantic salmon than for the eggs or older stages (Lacroix 1985a,b; Lacroix et al. 1985).

Interspecific Effects

Table 4 of Marmorek et al. (1984) summarizes the results of studies investigating the effects of pH and aluminum on aquatic biota; this table clearly shows the wide variability in tolerance to acidic precipitation processes. These results have been confirmed by Holtze and Hutchinson (1985) in an investigation of the tolerance of six fish species to pH and aluminum and by Freda (1985) who found that the lethal pH for different amphibian species varies from 3.4 to 4.5.

Interspecific differences in tolerance to organic acid conditions also exist and are manifested in the species composition of coloured, or brown waters. Freda and Dunson (in press) found very different amphibian species assemblages in coloured waters than in clear waters although this may be due strictly to pH differences. This has also been reported by Patrick et al. (1981) who report that humic lakes contain very different aquatic biota than are found in clear waters.

There are also individual differences in acid tolerance within a population. Again, referring to amphibian biota, Pough (1976) attributed observations of within-pond differences in egg mortality to genetic factors, but Pierce and Sikand (1985) suggest that these differences may be due to maternal factors or maturity of the egg when exposed to the acidification-related stresses.

Linkage 4.2 THE GROWTH, REPRODUCTION AND BEHAVIOUR OF BIOTA IS INFLUENCED BY THE CONCENTRATIONS OF MINERAL ACIDITY, THE CONCENTRATIONS OF ORGANIC ACIDITY, THE CONCENTRATIONS OF METALS, PRIMARILY ALUMINUM, AND THE AMELIORATING EFFECTS OF BASE CATIONS.

Freda and Dunson (in press) found significantly lower growth of amphibian larvae placed in lower pH water. They maintain that this more subtle impact may have important consequences, as Wilbur (1984, cited in

Freda and Dunson in press) has found that larval growth is the most important determinant of amphibian larval survival. Lacroix et al. (1985) recorded a significant retardation in the growth of Atlantic salmon fry up to 40-50 days after swim-up at pH 5.0 versus pH 6.0 in organic waters. Peterson and Martin-Robichaud (in press) report that Atlantic salmon alevin growth is lower at low pH, as is yolk to embryo biomass transfer. Also, Ingersoll et al. (1985) found adult brook trout growth was reduced at pH < 5.2 and that progeny of adult fish spawning in low pH, low Ca^{2+}, and high aluminum waters were less tolerant of acid stress than progeny of adults exposed to more neutral conditions.

It is reasonable to expect that biota inhabiting coloured waters can evolve different acid tolerance than populations of the same species inhabiting clear waters. To date, the only evidence for this comes from work on amphibians. Karns (1983, cited in Freda 1985) found that Rana sylvatica embryos from an acid bog were more tolerant of low pH than individuals of the same species from neutral waters. These results are supported by Cook (1983) and Pough (1976) in their studies on Ambystoma salamanders.

Other influences may compensate for acidification effects. For example, Kerekes et al. (1984), in a comparison of an acidic, eutrophic lake with an acidic oligotrophic lake, found that the acidic, eutrophic lake contained diverse and productive plant and vertebrate communities relative to the depauperate oligotrophic lake. Similar results have been reported by other workers (Howell, pers. comm.).

Behavioural Responses

Our understanding of the ability of aquatic biota to avoid severe acidic environments remains poor, likely because the appropriate behavioural and population distribution studies are logistically difficult to undertake. In a laboratory experiment, Gunn and Noakes (1985) found that lake trout and brook trout fry are able to detect lethal levels of H^+ and aluminum and use refugia provided for them. In a study directly relevant to waters with high organic acid levels, Beebee and Griffin (1977) discovered that Bufo calamita individuals which inhabit naturally acidic heathlands, are able to distinguish pH levels lethal to embryos but that individuals of the species living in neutral regions

were not. This suggests that particular populations of this species that have adapted to existing in high organic acid waters may have evolved a greater ability to detect deleterious environmental conditions. Finally, Kerekes et al. (1984) has observed blacknose dace utilizing only a high pH inflow area of a highly acidic lake in Nova Scotia.

It may be that biota are able to avoid areas of high acidification stresses, but there is some evidence that these stresses may be less important to biota than certain life history stage requirements. For example, Lacroix (pers. comm.) has observed Atlantic salmon, white suckers and alewives leaving areas of relatively low acidity stress and choosing sites with much higher acidity stress but containing good spawning habitat during their spawning periods, thereby also depositing eggs in areas of lethal pH conditions.

Linkage 4.3 THE GROWTH AND REPRODUCTION OF AQUATIC BIOTA IS INFLUENCED BY THE MORTALITY OF OTHER BIOTA PRESENT (COMPETITORS, PREDATORS, OR PREY).

Linkage 4.4 THE MORTALITY OF AQUATIC BIOTA IS INFLUENCED BY THE GROWTH, REPRODUCTION, AND BEHAVIOUR OF OTHER BIOTA PRESENT (COMPETITORS, PREDATORS, AND PREY).

Linkage 4.5 THE SPECIES COMPOSITION OF AN AQUATIC SYSTEM IS DETERMINED BY THE GROWTH, REPRODUCTION, AND MORTALITY OF ITS BIOTA.

The above Linkages in the hypothesis are more or less tautological (i.e., they are valid by definition). Almost completely unknown, however, are the implications of acidification influences on a particular component of the biota to competitive, predation processes and relationships within the system of concern. The discussion for these Linkages has been grouped into a single section because information and evidence for any particular Linkage is sparse and also pertains to the other Linkages.

Species shifts in response to acidification effects on particular parts of biota are well documented (e.g. Eriksson 1979, Yan and Strus 1980, Singer et al. 1983, and Bendell and McNicol in prep. b) and some examples particularly relevant to wetlands are worth noting. Recent surveys of waterfowl indicate that, while avian distribution may not be influenced directly by water chemistry, their distribution is strongly

tied to the distribution and abundance of their food supply (Kerekes et al. 1984, McNicol et al. 1985, Longcore et al. 1985). This is not surprising as many waterfowl species require access to a good food supply in the spring and summer seasons to reproduce and raise young. Similarly, Bendell et al. (1983) found that the diversity of fish species in a number of small headwater lakes in Ontario is dependent on the levels of aquatic vegetation. They speculate that shifts in the vegetation species composition may have large effects on the fish communities of those lakes. It is also possible that a reduction in populations of fish which feed on aquatic invertebrates may benefit waterfowl which utilize aquatic invertebrates for food by reducing inter-specific competition. Finally, observations of secondary production in highly organic waters (eg. Kerekes et al. in press) may be caused by increases in heterotrophic algae and bacteria which utilize both dissolved and particulate organic matter.

It was recognized that investigations into food chain effects of acidification would be worthwhile and useful, particularly since there is increasing evidence that predation and competition mediated interactions may cause large species shifts when a particular part of the biota is directly influenced by acidification. However, because of the complex nature of these trophic interactions, such research should strive to uncover consistent relationships in food chain effects, such as the response of piscivorous waterfowl to losses of fish prey as a result of acidification.

III SYNTHESIS OF RESEARCH RECOMMENDATIONS

III SYNTHESIS OF RESEARCH RECOMMENDATIONS

The preceding section summarizes the findings of our review of existing knowledge, including ideas presented at the December workshop. Throughout the discussions of the hypotheses, we have documented a variety of recommendations, some quite specific and others more general, for future research related to this issue. These recommendations are the product of the discussions that took place at the workshop, and generally reflect a consensus among the members of the subgroup that reviewed the relevant hypothesis. On the final day of the workshop, we attempted to summarize these recommendations into a single table (Table 2), to allow participants at the workshop to see how the recommendations that emerged from their own subgroup related to those suggested by other groups. The table organizes the research recommendations by hypothesis (rows) and according to the spatial scale on which the proposed research was intended to be carried out (columns).

The table is useful as a means for identifying overlap among disciplines in research needs and thus potential opportunities for collaboration and/or areas of duplication. In many cases similar research needs were proposed for more than one hypothesis (e.g., complexation constants measured in the lab: uplands, surface waters). Similarly, some research ideas were relevant to more than one spatial scale (e.g., measurements of SO_4^{2-} adsorption/retention capacity).

Since the rationales for the research needs presented in Table 2 are to be found in the preceding section, there is no need to review the table in detail here. Instead we briefly summarize some of the more critical issues that arose at the workshop out of the discussions of research needs.

Perhaps the most strongly voiced and widely supported research recommendation from the workshop concerned the need to more thoroughly examine existing data, particularly data gathered on regional scales. There was a very strong feeling that a great deal of valuable information is currently available (but often not easily accessible) that if thoughtfully analyzed, could provide extremely valuable insights into some of the key questions raised during the workshop discussions. For example,

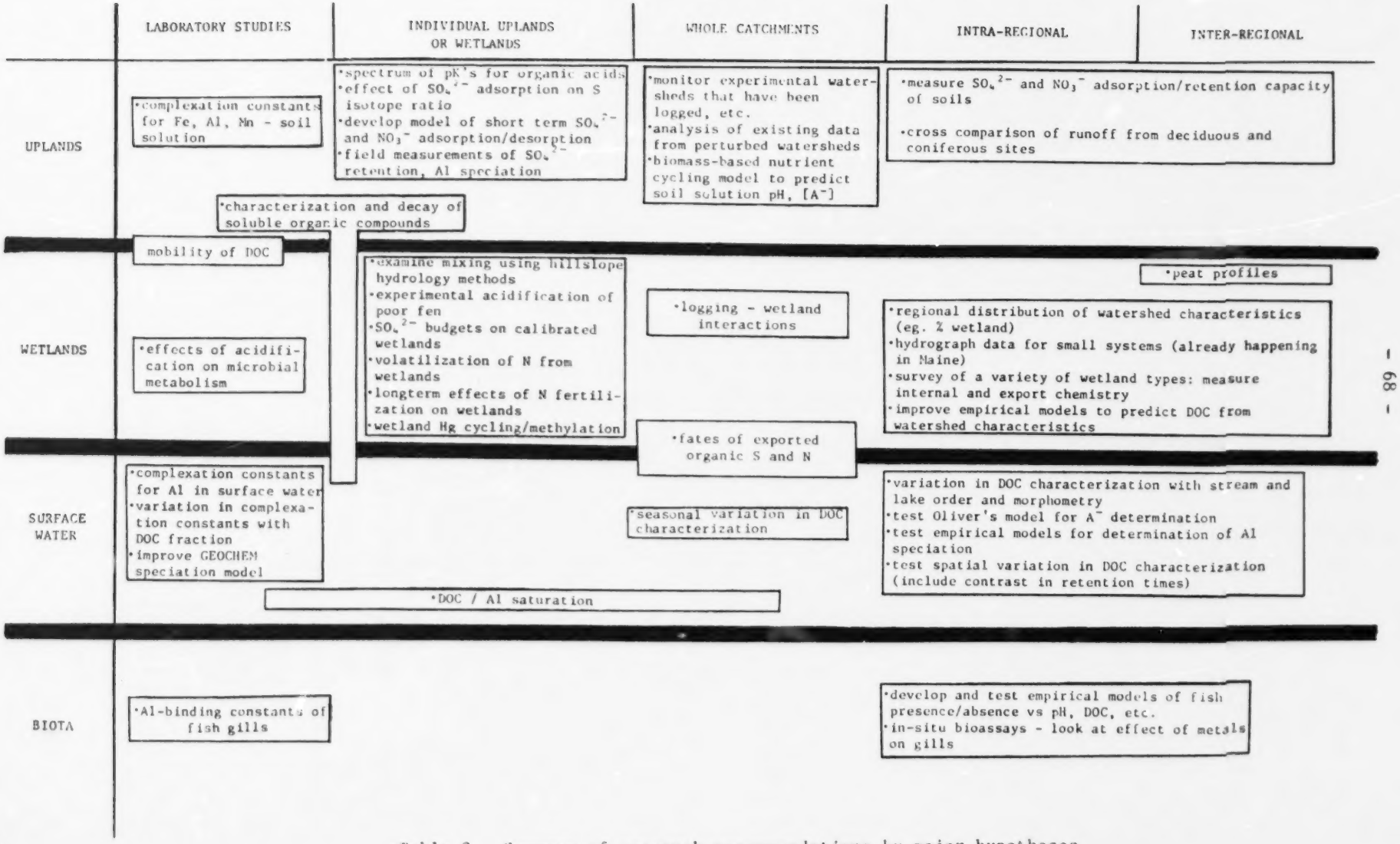

LABORATORY STUDIES
INDIVIDUAL UPLANDS OR WETLANDS
WHOLE CATCHMENTS
INTRA-REGIONAL
INTER-REGIONAL
UPLANDS
WETLANDS
SURFACE WATER
BIOTA
•complexation constants for Fe, Al, Mn - soil solution
•spectrum of pK's for organic acids
•effect of SO_4^{2-} adsorption on S isotope ratio
•develop model of short term SO_4^{2-} and NO_3^- adsorption/desorption
•field measurements of SO_4^{2-} retention, Al speciation
•monitor experimental watersheds that have been logged, etc.
•analysis of existing data from perturbed watersheds
•biomass-based nutrient cycling model to predict soil solution pH, [A⁻]
•measure SO_4^{2-} and NO_3^- adsorption/retention capacity of soils
•cross comparison of runoff from deciduous and coniferous sites
•characterization and decay of soluble organic compounds
mobility of DOC
•examine mixing using hillslope hydrology methods
•experimental acidification of poor fen
•SO_4^{2-} budgets on calibrated wetlands
•volatilization of N from wetlands
•longterm effects of N fertilization on wetlands
•wetland Hg cycling/methylation
•peat profiles
•logging - wetland interactions
•regional distribution of watershed characteristics (eg. % wetland)
•hydrograph data for small systems (already happening in Maine)
•survey of a variety of wetland types: measure internal and export chemistry
•improve empirical models to predict DOC from watershed characteristics
•effects of acidification on microbial metabolism
•fates of exported organic S and N
•complexation constants for Al in surface water
•variation in complexation constants with DOC fraction
•improve GEOCHEM speciation model
•seasonal variation in DOC characterization
•variation in DOC characterization with stream and lake order and morphometry
•test Oliver's model for A⁻ determination
•test empirical models for determination of Al speciation
•test spatial variation in DOC characterization (include contrast in retention times)
•DOC / Al saturation
•Al-binding constants of fish gills
•develop and test empirical models of fish presence/absence vs pH, DOC, etc.
•in-situ bioassays - look at effect of metals on gills

Table 2. Summary of research recommendations by major hypotheses and appropriate level of study.

plenty of surface water chemistry data now exists that could be combined with data on watershed land use to investigate correlations between these two sets of measures. Work of this type is already underway (e.g., Kessel-Taylor 1985), but several workshop participants felt that large information resources are not being adequately exploited.

It should be emphasized that this type of work does not subsume the need for future data gathering activities. In virtually all instances, analyses of existing data, particularly data not actually gathered to address the questions presently of interest, will yield little more than correlations that suggest an association between two or a number of parameters. Most of the time there are confounding factors, that can only be eliminated by more carefully controlled studies. Nevertheless, analyses of existing data can provide extremely valuable insights into what experimental research would be most informative, and can help to eliminate more speculative hypotheses.

A second major research issue concerns the necessary degree of characterization required to adequately describe DOC. There were rather divergent views on this, both among subgroups and among participants within subgroups. There was little disagreement, however, that the simplest (and analytically the least expensive) method of characterizing DOC that does not overlook important differences among fractions, or classes of compounds, is clearly the most desirable. The difficult question is deciding what differences are important.

Currently, it is clear that we have only a crude understanding at best, of how DOC affects biota, both directly and indirectly via interactions with metals. Similarly, there is limited evidence that the concentration of organic anions in surface waters can be predicted from knowledge of DOC and pH alone. As discussed under Hypothesis 3, however, such empirical models need a great deal more verification. On theoretical grounds one would expect differences in the acidity and ability to detoxify (via chelation) metals associated with different "types" of DOC. The central, unanswered question is just how significant these differences are in the context of effects on biota. The answer to this question clearly lies in developing a better understanding of how DOC interacts with biota. Since this understanding will not be obtained quickly, research on the characterization of DOC among regions, especially in

terms of complexation constants for metals, remains a high priority.

Although interest in wetlands, both as sources of runoff and as ecosystems unto themselves, has increased greatly in recent years, it is nevertheless important to stress the need for further studies of these unique and geographically abundant habitats. Their role in surface water chemistry is only beginning to be understood, and the initial evidence suggests it is a prominent one. As noted in Hypothesis 4, they also support a rich and unusual fauna (and flora), whose interactions with changes in water chemistry are largely unknown. Since at least some wetland types appear to be highly sensitive to mineral acid deposition, these fauna may be at considerable risk.

Finally, there is a major need to incorporate organic acids into existing acidification models, and to develop simple, but realistic models that link our current scientific understanding to relevant policy questions. While the research recommendations that have emerged from this review may (probably will) take years to complete, the need for answers is now. Rather than ignoring the fact that important policy decisions are being made today (including the decision not to act), the scientific community should be acting to ensure that decision makers are making their decisions using the best possible synthesis of our current understanding.

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